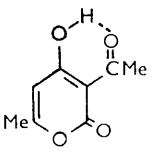
995. *Dehydroacetic Acid and its Derivatives.*

By J. D. Edwards, J. E. Page, and M. Pianka.

Dehydroacetic acid gave 2,6-bis-n-propylamino- and 2,6-bis-n-butylamino-hepta-2,5-dien-4-ones when treated with an excess of n-propylamine and n-butylamine, and *N*-methyl- and *N*-ethyl-4-lutidones when treated with excess of dilute methylamine and ethylamine. 2,6-Bisalkylaminohepta-2,5-dien-4-ones, prepared from diacetylacetone and excess of alkylamine, were cyclised to *N*-alkyl-4-lutidones. The mechanism of reaction between dehydroacetic acid and amines is discussed. The infrared and proton magnetic resonance spectra of these compounds and of bromodehydroacetic acid have been used to establish their structures.

Depending on reaction conditions, dehydroacetic acid (I) and primary aliphatic amines yield either the bases (III), 2,6-bis-n-alkylaminohepta-2,5-dien-4-ones (VIII), or 4-lutidones* (IX); [1-4] with primary aromatic amines dehydroacetic acid forms only bases (III) (Table 1).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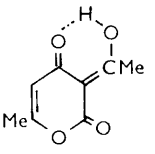
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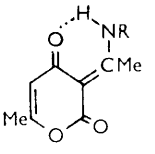
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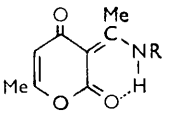
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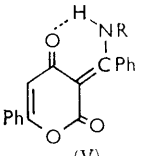
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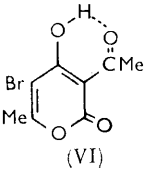
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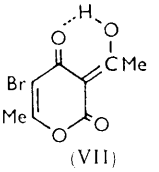
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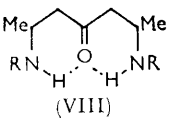

(VIII)

With one equivalent of primary alkylamines, dehydroacetic acid gives the bases (III; R = Me, Et, or Pr^n), with an excess of dilute methyl- or ethyl-amine, either at room temperature or on heating, it yields the lutidone (IX; R = Me or Et), but with an excess of dilute n-propyl- or n-butyl-amine, it gives the corresponding 2,6-bis-n-alkylaminohepta-2,5-dien-4-one [5] (III; R = Pr^n or Bu^n). Garratt [3] reported, in a Paper that appeared after the present Paper had been submitted for publication, that dehydroacetic acid with an excess of concentrated methylamine or ethylamine yielded the dienone (VIII; R = Me or Et).

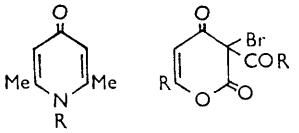
Diacetylacetone, with an excess of an alkylamine, gave the corresponding dienone (VIII; R = Me, Et, Pr^n, or Bu^n), from which, on treatment with water,[3,4] the lutidone (IX; R = Me or Et), or with alkali the lutidone (IX; R = Pr^n or Bu^n), was obtained. With an equivalent amount of an alkylamine, diacetylacetone gave the lutidone (IX) directly.

In order to test the validity of a referee's suggestion that the conversion of the base (III) into lutidone was instigated by internal participation [(XV) ⟶ (XVIII), cf. Cohen

* The results of Cook,[4] whose Paper appeared after the preparation of the present manuscript, are in agreement with ours.

[1] Iguchi, Hisatsune, Himeno, and Muraoka, *Chem. and Pharm. Bull.* (*Japan*), 1959, **7**, 323.
[2] Iguchi, Inoue, and Kurahashi, *Chem. and Pharm. Bull.* (*Japan*), 1961, **9**, 1016.
[3] Garratt, *J. Org. Chem.*, 1963, **28**, 1886.
[4] Cook, *Canad. J. Chem.*, 1963, **41**, 1435.
[5] Conley, Novoswiat, and Reid, *Chem. and Ind.*, 1959, 1157, prepared these dienones from 2,6-dimethyl-4-pyrone and primary aliphatic amines, but did not characterise them, nor did they report analytical data.

and Witkop [6]] we heated the base (III; R = Me) in water and alone, but less than 2% of the lutidone (IX; R = Me) was isolated. Since lutidones (IX) could not be formed directly from bases (III) we think that diaminoheptadienones (VIII) are intermediates in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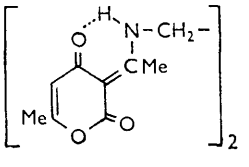
(X)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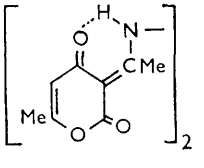
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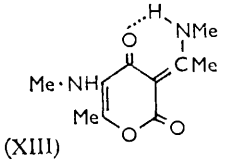
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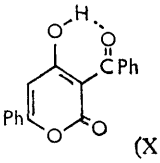
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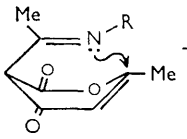
the conversion of dehydroacetic acid into lutidones (cf. Garratt [3] and Cook [4]). This view is supported by the following facts: (*a*) dehydroacetic acid and an excess of dilute methyl- or ethyl-amine yielded lutidones, (*b*) dehydroacetic acid and an excess of concentrated methyl- or ethyl-amine yielded diaminoheptadienones which could be converted into the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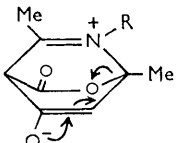
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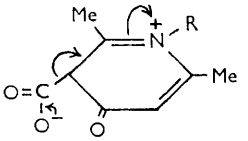
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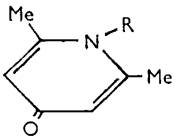
(XVIII)

lutidones on treatment with water [the formation of diaminoheptadienones (VIII; R = Pr^n or Bu^n) from dehydroacetic acid and dilute propyl- and butyl-amines may be due to the steric hindrance exerted by the alkyl groups which renders the formation of the lutidones more difficult].

Staudinger and Becker [7] ascribed structure (X; R = OMe) to the bromination product of 6-methoxy-3-methoxycarbonyl-2*H*-pyran-2,4(3*H*)-dione and structure (X; R = Me) to the bromination product of dehydroacetic acid. The compounds, surprisingly, gave a strong colour with ferric chloride solution. From examination of the infrared and proton magnetic resonance spectra of bromodehydroacetic acid we assigned to it structure (VI) [8] or possibly (VII).

Bromodehydroacetic acid gave, in the cold with one equivalent of ammonia, the ammonium salt, which, on heating, was converted into 3-α-aminoethylidene-5-bromo-6-methyl-2*H*-pyran-2,4(3*H*)-dione. This compound could also be obtained either by brominating the base (III; R = H) or by treating bromodehydroacetic acid with an excess of ammonia in the cold. However, when bromodehydroacetic acid was treated with an excess of methylamine, 6-methyl-5-methylamino-3-α-methylaminoethylidene-2*H*-pyran-2,4(3*H*)-dione (XIII) was obtained.

The amino-group of the base (III; R = H) could be replaced by a stronger amine, but the weaker base phenylhydrazine replaced amino-groups derived from much stronger amines.

Infrared and Proton Magnetic Resonance Spectra.—Our infrared and proton magnetic

[6] Cohen and Witkop, *Angew. Chem.*, 1961, **73**, 253.
[7] Staudinger and Becker, *Ber.*, 1917, **50**, 1016.
[8] Feist, *Ber.*, 1892, **25**, 315.

resonance (p.m.r.) measurements on dehydroacetic acid, (I) or (II), support Forsén and Nilsson's observations [9] (see also Iguchi *et al.*[1]), which suggest that dehydroacetic acid is completely enolised and has only one enolic form, probably (I) but possibly (II). Proton resonance measurements on solutions of dehydroacetic acid in concentrated sulphuric acid gave a similar result to that obtained for $CDCl_3$ solutions; in the acidic solutions, the two methyl peaks appeared at 6·87 and 7·31 τ, the olefinic proton at 3·15 τ, and the hydroxylic proton at −1·03 τ.

The infrared spectra of bromoform solutions of compounds (III; R = H, Me, Et, Pr^n, *o*-C_6H_4·NH_2, *p*-C_6H_4·NH_2, *p*-C_6H_4·NMe_2, *p*-C_6H_4Cl, *p*-C_6H_4Br, *p*-C_6H_4·Me, *p*-C_6H_4OH, NHPh, CH_2·CH_2OH) and of compounds (XI) and (XII) showed strong bands between 1708 and 1690 and between 1595 and 1560 cm.$^{-1}$ which were associated with the lactone carbonyl and the conjugated carbonyl groups, respectively (cf. Iguchi *et al.*[1] and Garratt [3]); these bands were distinguished from those associated with C=C linkages and ring vibration modes by examining solutions of dehydroacetic acid, aminodehydroacetic acid (III; R = H), and methylaminodehydroacetic acid (III; R = Me) in different solvents.[10,11] The bands for carbonyl groups moved to lower frequencies on going from ether, through dioxan, acetonitrile, and methylene chloride, to bromoform; the bands in the 1660—1596 cm.$^{-1}$ region associated with C=C linkages and ring vibration modes were substantially unchanged.

Aminodehydroacetic acid (III; R = H) is only slightly soluble in deuteriochloroform, but gives p.m.r. peaks for the two methyl groups at 7·37 and 7·87 τ and for the olefinic proton at 4·32 τ. In dimethyl sulphoxide solution, aminodehydroacetic acid shows a methyl peak at 7·92 τ (the second methyl peak is masked by solvent), an olefinic proton peak at 4·32 τ, and two broad single-proton peaks at 0·30 and −2·1 τ. The two single-proton peaks disappear on deuteration and are assigned to amino-protons; hydroxylic protons would be expected, as in dehydroacetic acid, to give sharp peaks. Aminodehydroacetic acid must, therefore, have structure (III; R = H),[8,12] which differs from that proposed by Iguchi *et al.*;[1] other structures either involve an enolic hydroxyl or are [cf. (IV; R = H)] unlikely on infrared evidence.

Infrared and p.m.r. measurements suggest similar structures for alkylaminodehydroacetic acid (III).[3] The p.m.r. spectrum of methylaminodehydroacetic acid (III; R = Me) in $CDCl_3$ has peaks at 7·85 (3H, doublet, J = 0·75 c./sec.; 6-Me), 7·32 (3H, singlet, ethylidene methyl), 6·80 (3H, doublet, J = 5·0 c./sec.; *N*-Me), 4·30 (1H, quartet, J = 0·75 c./sec.; olefinic proton), and −3·78 τ (1H, broad singlet, bonded amino-proton). On deuteration, the amino-proton peak disappears and the *N*-methyl doublet collapses to a singlet.[13,14] The spectrum of the picrate of methylaminodehydroacetic acid shows additional peaks at 0·97 and 0·03 τ for the two aromatic protons and the phenolic proton, respectively. The spectrum for ethylaminodehydroacetic acid (III; R = Et) is somewhat similar to that for methylaminodehydroacetic acid except that the methylene protons of the ethyl group give a multiplet at 6·45 τ, which collapses to a normal methylene quartet on deuteration; this confirms that the ethyl group and the amino-proton are on the same nitrogen atom. The aromatic bases of dehydroacetic acid were shown to have similar structures.

The infrared spectra of compound (XIV) and its basic derivatives (V; R = H or *p*-NH·C_6H_4·Me) and those of bromodehydroacetic acid (VI) and its amino-derivative and of compound (XIII) revealed the anticipated bands for lactone and conjugated carbonyl groups and for C=C linkages. P.m.r. measurements showed that compound (XIV) and its basic derivatives had similar structures to those of the dehydroacetic acid analogues. The position of the bromine atom in bromodehydroacetic acid is readily shown by nuclear

[9] Forsén and Nilsson, *Arkiv Kemi*, 1961, **17**, 523.
[10] Bellamy and Williams, *Proc. Roy. Soc.*, 1960, *A*, **255**, 22.
[11] Page and Staniforth, *J.*, 1962, 1292.
[12] Teist, *Annalen*, 1890, **257**, 353.
[13] Dudek and Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 2099.
[14] Dudek and Holm, *J. Amer. Chem. Soc.*, 1961, **83**, 3914.

magnetic resonance spectroscopy. Bromodehydroacetic acid in $CDCl_3$ shows sharp peaks at 7·52 and 7·30 τ for the two methyl groups and at −8·07 τ for the bonded hydroxyl proton; no olefinic protons are observed. Bromodehydroacetic acid must therefore have structure (VI), or possibly (VII). P.m.r. data showed that 3-α-aminoethylidene-5-bromo-6-methyl-2*H*-pyran-2,4(3*H*)-dione had a similar structure to that of aminodehydroacetic acid.

The infrared spectra of the 2,6-bisalkylaminohepta-2,5-dien-4-ones (VIII; R = Me, Et, Pr^n, or Bu^n) showed bands at 3200—3080 cm.$^{-1}$ (bonded NH), 1630—1625 and 1435—1520 cm.$^{-1}$ (C=C), and 1580—1566 cm.$^{-1}$ (conjugated C=O).[3] The structures were confirmed by p.m.r. measurements.[4] The 2,6-bismethylamino-analogue (VIII; R = Me) gave peaks at 8·20 (6H, doublet, J = 0·5 c./sec.; ethylidene methyl), 7·11 (6H, doublet, J = 5·5 c./sec.; *N*-Me), 5·30 (2H, quartet, J = 0·5 c./sec.; olefinic proton) and 0·10 τ (2H, broad singlet; bonded amino-proton); on deuteration, the amino-proton peak disappeared and the *N*-methyl doublet collapsed to a singlet.[13]

The *N*-alkyl-4-lutidones (IX; R = Me, Et, Pr^n, or Bu^n) in bromoform solution absorbed at 1640—1636 and 1570—1562 cm.$^{-1}$; peaks for water of crystallisation[15] appeared at 3680 and 1600 cm.$^{-1}$. *N*-Methyl-4-lutidone in deuteriochloroform showed p.m.r. peaks at 7·68 (6H, singlet; 2- and 6-Me), 6·50 (3H, singlet; *N*-Me) and 3·83 τ (2H, singlet; olefinic protons).

Experimental

Preparation of Basic Derivatives (III).—An equivalent quantity of an aqueous or ethanolic solution of methylamine or ethylamine was added to a suspension of dehydroacetic acid in water, warmed, if required, to bring it into solution and set aside at room temperature for 24 hr. When necessary, the mixture was filtered from a little solid, the filtrate evaporated to dryness (water-bath), and the residue recrystallised. The following compounds were prepared: (III; R = H),[16] (III; R = Me),[3] (III; R = Et).[3] The *n-propyl derivative* (III; R = Pr^n) was obtained as needles, m. p. 75—76° (from di-isopropyl ether) (Found: C, 62·9; H, 7·2; N, 6·6. $C_{11}H_{15}NO_3$ requires C, 63·2; H, 7·2; N, 6·7%). Under these conditions dehydroacetic acid and n-butylamine yielded an oil that could not be purified. Treatment of the base (III; R = Me) (0·5 g.) in water (10 ml.) with a saturated solution of picric acid in ethanol (10 ml.) gave the *picrate*, prisms, m. p. 129—130° (from ethanol) (Found: C, 44·15; H, 3·45; N, 13·45. $C_{15}H_{14}N_4O_{10}$ requires C, 43·9; H, 3·45; N, 13·7%).

With aromatic amines, an ethanolic solution of equivalent amounts of the amine and of dehydroacetic acid was heated under reflux for 1 hr. On cooling, the base crystallised and was filtered off and recrystallised. The properties of the new *bases* are summarised in the Table. Compound (III; R = CH_2·CH_2OH) was prepared by the method of Iguchi *et al.*[17] and compound (XII) by the method of Stollé.[18] All the bases could be converted into dehydroacetic acid by heating (steam-bath) with dilute hydrochloric acid.

Basic derivatives (III) of dehydroacetic acid.

R	M. p.	Solvent	Yield (%)	Crystal form	Found (%) N	Formula	Required (%) N
o-C_6H_4·NH_2	175°	Benzene	82	Fine needles	10·8	$C_{14}H_{14}N_2O_3$	10·8
p-C_6H_4·NH_2	210	Ethanol	79	Crystals	10·5	$C_{14}H_{14}N_2O_3$	10·8
p-C_6H_4·NMe_2.....	179—181	Ethanol	65	Needles	9·8	$C_{16}H_{18}N_2O_3$	9·8
p-C_6H_4Cl	138	Ethanol	91	Long needles	5·1	$C_{14}H_{12}ClNO_3$	5·1
p-C_6H_4Br	170	Ethanol	75	Platelets	4·3	$C_{14}H_{12}BrNO_3$	4·3
p-C_6H_4OH.....	219—220	Ethanol	69	Needles	5·4	$C_{14}H_{13}NO_4$	5·4
Compound (XI)	256—259		80	Scales	7·7	$C_{18}H_{20}N_2O_6$	7·8

Reaction of Dehydroacetic acid with Excess of Aromatic Amines.—Dehydroacetic acid (1·68 g., 0·01 mole) and aniline (2·8 g., 0·03 mole) were heated on a steam-bath for 18 hr. The base (III; R = Ph),[16] m. p. 119—121° (from propan-2-ol), was obtained (2·1 g., 82%). Under identical

[15] Bell, Shoffner, and Bauer, *Chem. and Ind.*, 1963, 1353, and references cited there.
[16] Oppenheim and Precht, *Ber.*, 1876, **9**, 1100.
[17] Iguchi, Inoue, and Kurahashi, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 385.
[18] Stollé, *Ber.*, 1905, **38**, 3030.

conditions, dehydroacetic acid and *p*-toluidine yielded the base (III; R = *p*-C_6H_4·Me) (2·2 g., 81·5%),[19] m. p. 154° (from ethanol). No precipitate formed on the addition of picric acid to the mother-liquors in either case, indicating absence of lutidone (IX).

Preparation of N-*Alkyl*-4-*lutidones*.—N-*Methyl*-4-*lutidone*. Aqueous methylamine (25% w/w; 20 g., 0·17 mole) and dehydroacetic acid (4 g., 0·024 mole) were warmed for 15 min. (water-bath) and the white crystalline solid that precipitated on standing at room temperature for 24 hr. was filtered off and dried *in vacuo* (P_2O_5). It was *N*-methyl-4-lutidone (2·85 g., 86·6%), m. p. 245—246°,[3] not depressed by the product obtained from equivalent proportions of diacetylacetone and methylamine. When dehydroacetic acid (4 g.) and aqueous methylamine (25% w/w; 20 g.; diluted with 100 ml. of water) was kept for 3 days at room temperature the lutidone (IX; R = Me) was obtained (1·67 g.). On recrystallisation from water the trihydrate, m. p. 108—110°,[4] was obtained. The lutidone was also obtained when the base (III; R = Me) (1 g.), in water (5 ml.), was treated with aqueous methylamine (26·5% w/w; 5 g.).[4] The crystals that separated after 1 day were filtered off and dried *in vacuo* (P_2O_5) (0·55 g., 59·4%), m. p. 244—245°, not depressed by *N*-methyl-4-lutidone.

N-*Ethyl*-4-*lutidone*. Ethanolic ethylamine (33% w/w; 27·3 g., 0·2 mole) was added to a suspension of dehydroacetic acid (4·2 g., 0·025 mole) in water (100 ml.). After 1 day the solution was concentrated by heating (water-bath). The residue was crystallised from ethyl acetate yielding the lutidone (IX; R = Et) hydrate, m. p. 69—71°, from which the anhydrous compound was obtained by drying *in vacuo* (P_2O_5), m. p. 160—163·5°, not depressed by the product obtained from equivalent proportions of diacetylacetone and ethylamine. Some base (III; R = Et) was also isolated from the reaction mixture.

N-*Alkyl*-4-*lutidones from diacetylacetone and alkylamines*. When equivalent proportions of diacetylacetone and alkylamines were heated for several hours on a water-bath, *N*-alkyl-4-lutidones (IX) were obtained, and were dried *in vacuo* (P_2O_5). The following were prepared: *N*-methyl-4-lutidone; *N*-ethyl-4-lutidone;[4] *N*-n-propyl-4-lutidone monohydrate;[20] *N*-n-butyl-4-lutidone monohydrate, white prisms (from benzene), m. p. 88—89° (lit.,[20] 109°) (Found: C, 66·3; H, 9·6; N, 7·1. Calc. for $C_{11}H_{19}NO_2$: C, 67·2; H, 9·6; N, 7·1%).

Picrates of N-*Alkyl*-4-*lutidones*.—These were obtained by adding a solution of picric acid in ethanol to solutions of the lutidones (IX) in ethanol. They were crystallised from ethanol. The following were prepared: *N*-methyl-4-lutidone picrate;[21] *N*-ethyl-4-lutidone picrate;[21] N-*n-propyl*-4-*lutidone picrate*, long prisms, m. p. 175—176° (Found: C, 49·1; H, 5·2. $C_{16}H_{18}N_4O_8$ requires C, 48·7; H, 4·6%); N-*n-butyl*-4-*lutidone picrate*, needles, m. p. 151—152° (Found: C, 49·9; H, 4·9. $C_{17}H_{20}N_4O_8$ requires C, 50·0; H, 4·9%).

Preparation of 2,6-*Bisalkylaminohepta*-2,5-*dien*-4-*ones* (VIII).—(*a*) *Using an excess of n-propylamine*. n-Propylamine (5·9 g., 0·1 mole) was added to a suspension of dehydroacetic acid (4·2 g., 0·025 mole) in water (20 ml.). The solid that precipitated after 1 day was filtered off (1·8 g., 29·1%), m. p. 77—78°, not depressed by 2,6-bis-n-propylaminohepta-2,5-dien-4-one obtained from (*c*). From the filtrate the base (III; R = Pr^n) (1·75 g.), m. p. 75—76°, was obtained. Similar results were obtained when aqueous propylamine (25% w/w; 39·3 ml., 0·17 mole) and dehydroacetic acid (4 g., 0·024 mole) were heated on a steam-bath for 4 hr. Some lutidone (IX; R = Pr^n) was isolated from the filtrate.

(*b*) *Using an excess of n-butylamine*. The conditions were as above, but n-butylamine (7·3 g., 0·1 mole) was used. The solid that precipitated after 3 days was filtered off (3·7 g., 53·1%), m. p. 64—65°, not depressed by 2,6-bis-n-butylaminohepta-2,5-dien-4-one obtained from (*c*). Some *N*-n-butyl-4-lutidone was isolated from the filtrate. Similar results were obtained when dehydroacetic acid was heated with butylamine (33% in ethanol; 7 equivalents) for 3 hr.

(*c*) *Diacetylacetone and excess of alkylamines*. A mixture of diacetylacetone, in a suitable solvent, and two equivalents of the amine (four in the case of methylamine) was set aside at room temperature for 1—2 days. The solvent was evaporated and the residue crystallised. The followed were prepared: 2,6-bismethylamino-,[3] 2,6-bisethylamino-,[4] 2,5-*bis*-*n*-*propylamino*-, needles, m. p. 77—78° [from light petroleum (b. p. 60—80°)] (Found: C, 69·2; H, 10·6; N, 12·5. $C_{13}H_{24}N_2O$ requires C, 69·6; H, 10·7; N, 12·5%), and 2,5-*bis*-*n*-*butylamino*-*hepta*-2,5-*dien*-4-*one*, large needles, m. p. 64—65° [from light petroleum (b. p. 60—80°)] (Found: C, 71·4; H, 11·2; N, 11·0. $C_{15}H_{28}N_2O$ requires C, 71·4; H, 11·1; N, 11·1%).

[19] Buelow, *Ber.*, 1908, **41**, 4165.
[20] Chauvelier, *Bull. Soc. chim. France*, 1954, 734.
[21] Iguchi and Inoue, *Chem. and Pharm. Bull.* (*Japan*), 1963, **11**, 390.

Conversion of 2,6-*Bisalkylaminohepta*-2,5-*dien*-4-*ones into* N-*Alkyl*-4-*lutidones*.—(*a*) *With potassium hydroxide.* To compound (VIII; R = Pr^n or Bu^n) (0·5 g.), in ethanol (10 ml.), potassium hydroxide pellets (0·5 g.) were added and the mixture was heated gently until a clear solution resulted. This was kept in a stoppered flask for several days at room temperature and then concentrated (steam-bath). The solid that separated on cooling was filtered off, washed with a little water, and dried *in vacuo* (P_2O_5). It gave no depression of m. p. with the corresponding *N*-alkyl-4-lutidone.

(*b*) *With picric acid.* On adding an ethanolic solution of picric acid to an ethanolic solution of the dienones (VIII) the picrate of the corresponding *N*-alkyl-4-lutidone was obtained.

Attempted Conversion of the Base (III; R = Me) *into the Lutidone* (IX; R = Me).—(*a*) The base (3 g.), dissolved in water (30 ml.), was heated under reflux for 2 hr. The water was evaporated and the residue was recrystallised yielding 2·1 g. of the original base (III; R = Me). From the filtrate a minute amount (0·1 g.) of the picrate of the lutidone (IX; R = Me) was obtained on the addition of ethanolic picric acid.

(*b*) The base (3·4 g.) was heated in an air-bath at 230° for 3 hr. The resulting black tar was extracted with boiling carbon tetrachloride, and the residue was extracted with boiling ethyl acetate. The gum (0·15 g.) that precipitated from the ethyl acetate extract on cooling, was dissolved in hot water (2 ml.) and treated with charcoal, then with ethanolic picric acid. Only 0·15 g. of the picrate of the lutidone (IX; R = Me) was obtained.

Replacement of R in the Bases (III).—To the base (III; R = *p*-C_6H_4·Me), in ethanol, was added aqueous ammonia and the solution was concentrated by heating (water-bath). Aminodehydroacetic acid (III; R = H), m. p. 210—211°, crystallised out from the solution. This compound was recovered unchanged after heating it with *p*-toluidine in ethanol.

Equivalent amounts of aminodehydroacetic acid (III; R = H) (1·67 g.; 0·01 mole) and n-propylamine (0·59 g.; 0·01 mole), in ethanol, were mixed and kept for 1 day at room temperature. The ethanol was removed under reduced pressure leaving an oil (2 g.) which was extracted with di-isopropyl ether. From the extract, the base (III; R = Pr^n), m. p. 75—76°, crystallised out (1·1 g., 52·6%).

Similarly, the base (III; R = Me) was prepared from base (III; R = *p*-C_6H_4·Me) and methylamine. Phenylhydrazine was added to the base (III; R = *p*-C_6H_4·Me, H, Me, or Pr^n), dissolved in ethanol. The base (III; R = NHPh), prisms, m. p. 206—206·5° (decomp.),[19] was obtained in each case.

3-α-*Aminoethylidene*-5-*bromo*-6-*methyl*-2H-*pyran*-2,4(3H)-*dione*.—Ammonia (10 ml.; *d* 0·88) was added to a suspension of bromodehydroacetic acid (VI) (2·47 g.) prepared by the method of Feist,[8] in water (10 ml.), and warmed (steam-bath) until a clear solution resulted. After 25 min. water (10 ml.) was added, and the solid that crystallised out was filtered off. The *dione* was obtained as long white prisms (1·67 g.), m. p. 240—241° (decomp.) (from ethanol) (Found: N, 5·6. $C_8H_8BrNO_3$ requires N, 5·7%). This compound was also obtained as follows. To aminodehydroacetic acid (III; R = H) (3·34 g., 0·02 mole), in chloroform (8 ml.), was added bromine (3·6 g., 0·02 mole), in chloroform (2 ml.). There was a mildly exothermic reaction. The solvent was allowed to evaporate off at room temperature leaving a residue which, on recrystallisation from ethanol then methanol, yielded a solid, m. p. 238—239·5° (decomp.).

6-*Methyl*-5-*methylamino*-3-α-*methylaminoethylidene*-2H-*pyran*-2,4(3H)-*dione* (XIII).—Ethanolic methylamine (33% w/w; 7·52 g.) was added to a suspension of bromodehydroacetic acid (VI) (2·47 g.) in water (20 ml.). The solid that separated from the solution after 1 day at room temperature was filtered off, washed with aqueous ethanol, and dried *in vacuo* (P_2O_5). The *compound* was obtained as clusters of needles (1·35 g.), m. p. 188° (from ethanol) (Found: C, 57·05; H, 6·65; N, 13·2. $C_{10}H_{14}N_2O_3$ requires C, 57·15; H, 6·65; N, 13·35%).

3-α-*Aminobenzylidene*-6-*phenyl*-2H-*pyran*-2,4(3H)-*dione* (V; R = H).—This was obtained from the dione (XIV) [22] and ammonia as white plates, m. p. 281—282° (from methanol then benzene) (Found: C, 74·5; H, 4·45; N, 4·4. Calc. for $C_{18}H_{13}NO_3$: C, 74·25; H, 4·45; N, 4·8%). Feist [23] reported m. p. 267° and described the compound as 2,6-diphenyl-4-pyridone. Petrenko-Kritschenko and Schoettle [24] described this compound as 3-benzoyl-6-phenylpyrid-2,4(1,3*H*)-dione. 6-*Phenyl*-3-α-p-*tolylaminobenzylidene*-2H-*pyran*-2,4(3H)-*dione* (V; R = *p*-C_6H_4·Me) was

[22] Bayer and Perkin, *Ber.*, 1884, **17**, 64.
[23] Feist, *Ber.*, 1890, **23**, 3736.
[24] Petrenko-Kritschenko and Schoettle, *Ber.*, 1911, **44**, 2826.

obtained from the dione (XIV) and *p*-toluidine as felt needles, m. p. 200—202° (from ethanol) (Found: C, 78·5; H, 5·15; N, 3·7. $C_{25}H_{19}NO_3$ requires C, 78·7; H, 5·0; N, 3·65%).

Spectroscopic Measurements.—The infrared [11] and p.m.r. measurements [25] were conducted as described previously. The infrared spectra of twenty-nine compounds will be deposited in the D.M.S. Scheme (Butterworths Scientific Publications, London) and will bear the numbers 11971—11999.

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[25] Green, Page, and Staniforth, *J.*, 1964, 144.