689. *The Conversion of Sucrose into Pyridazine Derivatives. Part X. The Properties and Structure of* 3-*Methyl*-6-*pyridazone*, 1 : 3-*Dimethyl*-6-*pyridazone, and Some Derivatives of Pyridazine.*

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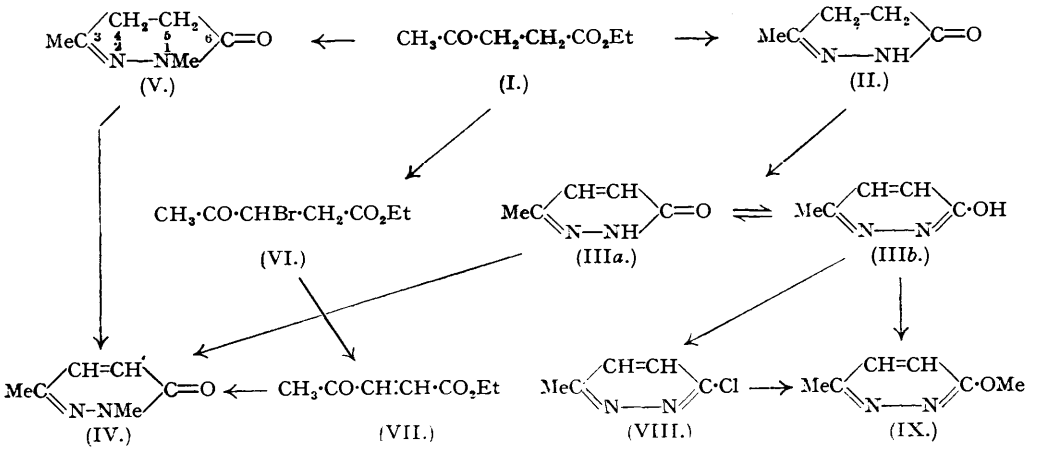
Proof of the structure of 1 : 3-dimethyl-6-pyridazone is provided. The possible existence of tautomeric forms of 3-methyl-6-pyridazone has been investigated by ultra-violet and infra-red absorption spectra measurements. The ultra-violet absorption spectra of numerous pyridazine derivatives are reported.

Earlier work in this series has been directed towards the preparation of pyridazine derivatives of possible use as chemotherapeutic agents. The present communication deals with the chemistry of 3-methyl-6-pyridazone * and 1 : 3-dimethyl-6-pyridazone,* which are important intermediates in these syntheses.

3-Methyl-6-pyridazone (III*a* and *b*) was first prepared by Poppenberg (*Ber.*, 1901, **34**, 3257) by the dehydrogenation of 1 : 3 : 5 : 6-tetrahydro-6-keto-3-methylpyridazine (II) with bromine in acetic acid under anhydrous conditions, and the yield was raised to practically quantitative level by Overend and Wiggins (*J.*, 1947, 239). Treatment of 3-methyl-6-pyridazone (III) with methyl iodide and sodium methoxide afforded a product which Poppenberg designated as 1 : 3-dimethyl-6-pyridazone (IV) but he adduced no evidence in support of this formulation. Since 3-methyl-6-pyridazone may exist in tautomeric forms (III*a* and *b*) it seemed important that proof of this structure should be obtained. The reaction was repeated and a product clearly identical with

* The numbering now used is shown in (V). Previously these compounds were numbered as 6-methyl-3-pyridazone and 2 : 6-dimethyl-3-pyridazone.

that described by Poppenberg obtained, although the melting point is 10° higher than that previously reported. The same compound was also prepared by treating (III) with methyl



sulphate and 30% aqueous sodium hydroxide. In addition (IV) was prepared by two alternative methods which prove its structure. Ethyl lævulate (I) with methylhydrazine yielded a liquid tetrahydroketodimethylpyridazine which by the method of preparation must possess the structure 1 : 3 : 5 : 6-tetrahydro-6-keto-1 : 3-dimethylpyridazine (V). Dehydrogenation with bromine in acetic acid under anhydrous conditions afforded the monohydrobromide of the dimethylpyridazone (IV) identical with that obtained from 3-methyl-6-pyridazone as above. Secondly, ethyl β-acetylacrylate (VII) and methylhydrazine also gave (IV); this procedure prefixed the ethylene linkage in the product. Ethyl β-acetylacrylate (VII) was obtained from ethyl lævulate (I) by conversion into ethyl β-bromolævulate (VI) (Conrad and Guthzeit, *Ber.*, 1884, **17**, 2285) which with one molecular proportion of sodium acetate afforded (VII) in an overall yield of 39%; the best overall yield of methods previously reported was 24%.

3-Methyl-6-pyridazone is able to react in its tautomeric form (III*b*) and can be chlorinated by either phosphorus oxychloride (Poppenberg, *loc. cit.*; Overend and Wiggins, *loc. cit.*) or phosphorus pentachloride (Overend and Wiggins, *loc. cit.*) to yield 3-chloro-6-methylpyridazine (VIII). Reduction of this either by hydrogen iodide and red phosphorus or by catalytic hydrogenation over Raney nickel gave 3-methylpyridazine. This was a basic compound which formed a monohydrochloride. 3-Methoxy-6-methylpyridazine (IX), isomeric with Poppenberg's 1 : 3-dimethyl-6-pyridazone was obtained by treating 3-chloro-6-methylpyridazine with sodium methoxide in methyl alcohol. It was a liquid but formed a crystalline hydrochloride; it was also obtained, albeit in poor yield, by the action of ethereal diazomethane on 3-methyl-6-pyridazone.

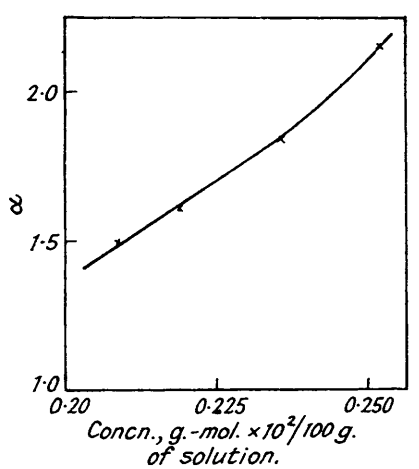
The chemistry of compound (II) is also complicated by the fact that it could undergo keto–enol, lactam–lactim, and methylene–imine tautomeric changes. Deductions from chemical evidence concerning these tautomeric interconversions are difficult to make, because of the instability of tetrahydro-6-ketopyridazine derivatives towards certain reagents, especially those acidic in nature. To supplement the inconclusive chemical evidence the ultra-violet absorption spectra of a large number of pyridazine, 6-pyridazone, and tetrahydro-6-keto-pyridazine derivatives have been measured.

Very little work has been carried out on the measurement of the absorption spectra of six-membered 1 : 2-diazine structures, being limited to that of Biquard and Grammaticakis (*Bull. Soc. chim.*, 1940, **7**, 766) and more recently of Evans and Wiselogle (*J. Amer. Chem. Soc.*, 1945, **67**, 60) who described the ultra-violet absorption spectrum of pyridazine in solution in water and in hexane and showed this to be affected by the solvent used. Each of these workers reported very few measurements and it was impossible to draw any conclusion from them regarding the various possible tautomeric structures. Consequently in the present communication an attempt has been made to systematise the ultra-violet absorption spectra data of cyclic six-membered 1 : 2-diazine derivatives. The measurements were made on a Hilger quartz spectrograph in aqueous or alcoholic solution. From the data listed in the Table it is clear that the absorption spectrum of 3-methyl-6-pyridazone is more akin to those of the pyridazone derivatives substi-

	Compound.	Solvent.	Concn., mg. %.	$\lambda_{max.}$, A.	$\varepsilon_{max.}$
A.	1 : 4 : 5 : 6-Tetrahydro-6-keto-3-methylpyridazine	H_2O	3·7	2430	6000
	1 : 4 : 5 : 6-Tetrahydro-6-keto-1 : 3-dimethylpyridazine	H_2O	1·5	2460	5000
	1 : 4 : 5 : 6-Tetrahydro-6-keto-3-methyl-2-phenylpyridazine	EtOH	1·9	2370	11,000
	Acetylated 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methylpyridazine	H_2O	22·6	<2300	—
B.	3-Methyl-6-pyridazone	H_2O	3·7	2850	2200
	3-Methyl-6-pyridazone monohydrochloride	H_2O	3·96	2820	3000
	6-Pyridazone	H_2O	2·2	2800	3550
	1 : 3-Dimethyl-6-pyridazone	EtOH	7·48	2940	2460
	1-Ethyl-3-methyl-6-pyridazone	H_2O	3·03	2900	3000
	3-Methyl-1-phenyl-6-pyridazone	EtOH	2·87	3130	6500
	4-Chloro-1 : 3-dimethyl-6-pyridazone [1]	EtOH	3·82	3060	3750
	4-Amino-1 : 3-dimethyl-6-pyridazone [2]	EtOH	3·99	2780	6500
	4 : 5-Dichloro-1 : 3-dimethyl-6-pyridazone [1]	EtOH	3·99	3060	4000
	4 : 5-Diacetamido-1 : 3-dimethyl-6-pyridazone [2]	H_2O	3·16	2780	14,000
	1-Hydroxymethyl-3-methyl-6-pyridazone [3]	EtOH	4·2	2890	3340
	1-Hydroxymethyl-6-pyridazone [3]	EtOH	6·15	2820	1500
	1-Benzyl-3-methyl-6-pyridazone [3]	EtOH	8·5	3010	1620
	1-Methyl-6-pyridazone [3]	EtOH	9·37	2860	1540
C.	Di-(3-methylpyridaz-6-on-1-yl)phenylmethane [3]	EtOH	6·7	2980	4760
	Di(pyridaz-6-on-1-yl)phenylmethane [3]	EtOH	1·43	2930	5350
D.	3-Methylpyridazine	EtOH	10·6	2510 3100	1300 400
	3-Amino-6-methylpyridazine	H_2O	5·0	2290 2990	7400 2000
	3-Amino-6-methylpyridazine monohydrochloride	H_2O	7·6	2280 2970	7000 1700
	3-Acetamido-6-methylpyridazine	H_2O	2·16	2340	13,000
	3-Chloro-6-methylpyridazine	H_2O	12·9	2630	1600
	3-Chloro-6-methylpyridazine monohydrochloride	H_2O	8·28	2620	1600
	3-Methoxy-6-methylpyridazine	EtOH	4·5	2710	2000
	3-Methoxy-6-methylpyridazine monohydrochloride	EtOH	9·92	2720	2000
	3-Benzyloxy-6-methylpyridazine [3]	EtOH	8·4	2730	1480

[1] Homer, Gregory, and Wiggins, *J.*, 1948, 2191. [2] Homer, Gregory, Overend, and Wiggins, *J.*, 1948, 2195. [3] Gregory, Hills, and Wiggins, *J.*, 1949, 1248.

tuted at position 1 (Sections *B* and *C* of the Table), than it is to those of the pyridazine derivatives (Section *D*). 6-Pyridazone itself also seems to behave similarly. This means that both 6-pyridazone and 3-methyl-6-pyridazone exist normally to a large extent in the lactam form. On addition of sodium hydroxide to 3-methyl-6-pyridazone the position of maximum absorption moves from 2850 ($\varepsilon_{max.}$ 2200) to 3000 A. ($\varepsilon_{max.}$ 3000), that is, still nearer to that of most of the 1-substituted 6-pyridazone derivatives and more removed from that of the pyridazine derivatives. On addition of hydrochloric acid to the solution of the sodium derivative of 3-methyl-6-pyridazone, the position of maximum absorption reverts to its original position ($\lambda_{max.}$ 2850 A., $\varepsilon_{max.}$ 2200). Consequently it seems likely that 3-methyl-6-pyridazone under the influence of sodium hydroxide reacts in its lactam form to give an *N*-sodium derivative and not in its lactim form to give the salt of an enol.



It is unlikely that 1 : 4 : 5 : 6-tetrahydro-6-keto-3-methylpyridazine exists normally as lactim, since there is little difference between its spectrum and those of the 1 : 3-dimethyl and the 3-methyl-1-phenyl isomer. For this group of compounds, however, it is impossible to state whether enol or keto-forms are present since all are able to undergo such transformations. To decide this point infra-red measurements were kindly carried out for us by Dr. H. P. Koch on (II), (V), (IV), and (III). The results indicated that all four compounds existed in the carbonyl form. (V) and (IV) exhibited carbonyl absorption at 1680 and 1670 cm.$^{-1}$ respectively in carbon disulphide solution. (II) and (III) were insoluble in carbon disulphide but absorbed

at 1670 and 1685 cm.$^{-1}$ respectively in chloroform solution and at 1635 and 1650 cm.$^{-1}$ respectively in the crystalline state. From these results it is evident that 1 : 3 : 5 : 6-tetrahydro-6-keto-3-methylpyridazine exists as (II) (keto–lactam) and 3-methyl-6-pyridazone as (III*a*) and not normally as (III*b*) although in certain circumstances it can react in the latter form (Overend and Wiggins, *J.*, 1947, 239).

The relative insolubility and the frequency shifts in the infra-red region of the spectrum of 3-methyl-6-pyridazone and its tetrahydro-derivative in the crystalline state appear to indicate dimeric complex formation *via* strong hydrogen bonding (cf. Koch, *J.*, 1949, 401). The molecular weight of anhydrous 3-methyl-6-pyridazone, measured in benzene solution (cryoscopic method), increased as the concentration of the solid in the solvent increased (see Fig.), indicating that association did take place (cf. Hunter, *Chem. and Ind.*, 1941, 32).

Experimental.

1 : 3-*Dimethyl*-6-*pyridazone*.—(*a*) Anhydrous 3-methyl-6-pyridazone (2·1 g.), methyl iodide (2·71 g.), and sodium methoxide (1·03 g.) in dry methyl alcohol (75 c.c.) were boiled under reflux for 1 hour and then evaporated to dryness. Aqueous potassium hydroxide was added until the solution was alkaline, then the mixture was extracted with benzene. The extract was dried ($MgSO_4$) and the solvent removed by evaporation. The oily residue solidified on storage and, recrystallised from alcohol–ether, formed white cubes, m. p. 50—51° (Found : C, 57·7; H, 6·1; N, 23·0. Calc. for $C_6H_8ON_2$: C, 58·1; H, 6·4; N, 22·6%).

(*b*) 3-Methyl-6-pyridazone (0·64 g.), methyl sulphate (0·6 g.), and 30% aqueous sodium hydroxide solution (0·6 c.c.) were warmed together at 70° for 2 hours. The solution was evaporated to dryness, and the residue made alkaline with sodium hydroxide solution and extracted with benzene. The extract was dried ($MgSO_4$) and the solvent removed by evaporation. An oil remained which was induced to crystallise. It recrystallised from light petroleum (b. p. 40—60°) in colourless plates (0·21 g., 30%), m. p. 50° alone or in admixture with the 1 : 3-dimethyl-6-pyridazone prepared above. This compound was soluble in water at 15° to the extent of 9·36 g. per 100 c.c. of solution. Other preparative methods are recorded by Homer, Gregory, and Wiggins (*J.*, 1948, 2191). 1 : 3-Dimethyl-6-pyridazone (0·1 g.) was dissolved in alcohol (5 c.c.), and dry hydrogen bromide bubbled through the solution which was cooled to 0°. On addition of ether a solid separated and was collected. This, recrystallised from alcohol–ether, formed long colourless needles, m. p. 150°, of 1 : 3-*dimethyl*-6-*pyridazone monohydrobromide* (Found : C, 35·0; H, 4·3. $C_6H_8ON_2$,HBr requires C, 35·1; 4·4%). The salt was deliquescent and soon decomposed on exposure to the atmosphere.

1-*Ethyl*-3-*methyl*-6-*pyridazone*.—Anhydrous 3-methyl-6-pyridazone (4·6 g.), ethyl iodide (5·0 g.), and sodium (0·98 g.) in dry ethyl alcohol (50 c.c.) were boiled under reflux for 1 hour and then evaporated to dryness, and the residue was extracted with benzene. Evaporation of the extract afforded a liquid which was distilled under atmospheric pressure. The *product* (1·65 g., 29%) was collected as a colourless liquid, b. p. 229—230°, $n^{16\cdot5}$ 1·5174 (Found : C, 60·7; H, 7·0. $C_7H_{10}ON_2$ requires C, 60·9; H, 7·2%).

1-Ethyl-3-methyl-6-pyridazone (0·1 g.) was dissolved in alcohol (5 c.c.) and dry hydrogen chloride passed into the solution. On addition of ether a solid was precipitated. This, recrystallised from alcohol–ether, formed the *monohydrochloride* as a deliquescent solid of indefinite m. p. (Found : Cl, 20·0. $C_7H_{10}ON_2$,HCl requires Cl, 20·4%).

3-*Methoxy*-6-*methylpyridazine*.—3-Chloro-6-methylpyridazine (2·0 g.) was dissolved in dry methyl alcohol (150 c.c.) containing sodium (5 g.). After the solution had been boiled under reflux for 2 hours and evaporated to dryness, excess of aqueous potassium hydroxide was added and the solution extracted with benzene. The extract was dried ($MgSO_4$) and the benzene then removed by evaporation. The residue distilled as a colourless liquid (0·7 g., 36·8%) (basic to litmus) which soon became red, b. p. 210°, n^{21} 1·5014 (a large amount of resinous material remained in the flask) (Found : N, 22·5. $C_6H_8ON_2$ requires N, 22·6%). The 3-*methoxy*-6-*methylpyridazine* (0·1 g.) was dissolved in alcohol (5 c.c.) and dry hydrogen chloride was bubbled through the cooled solution. After evaporation to dryness a crystalline *hydrochloride* was obtained, which crystallised from absolute alcohol in large colourless plates, m. p. 131—132° (Found : C, 44·6; H, 5·8. $C_6H_8ON_2$,HCl requires C, 44·8; H, 5·6%).

Treatment of 3-*Methyl*-6-*pyridazone with Diazomethane*.—3-Methyl-6-pyridazone monohydrate (7·0 g.) was dehydrated by heating it at 140° under diminished pressure and was then dissolved in dry methyl alcohol (150 c.c.). Excess of diazomethane in ether was added and the mixture was set aside. Effervescence occurred. The excess of diazomethane was removed by distillation with the solvent and the residue extracted with ether. An insoluble residue was unchanged 3-methyl-6-pyridazone (4·5 g.). The ethereal extract yielded an oil on evaporation and this distilled as a pale yellow liquid (0·3 g.), b. p. 210—215°, n^{21} 1·5010. Its hydrochloride had m. p. 131°, alone or in admixture with 3-methoxy-6-methylpyridazine monohydrochloride.

1 : 4 : 5 : 6-*Tetrahydro*-6-*keto*-1 : 3-*dimethylpyridazine*.—Methylhydrazine sulphate (15·13 g.) in water (20 c.c.) was cooled in ice, and sodium hydroxide (9·0 g.), also dissolved in water (20 c.c.), slowly added. The solution was then evaporated to dryness and the aqueous distillate added to ethyl lævulate (15 g.). Sufficient ethyl alcohol was added to make the mixture homogeneous, and it was then boiled under reflux for 1 hour. Thereafter the solvents were removed under diminished pressure, and the 1 : 4 : 5 : 6-*tetrahydro*-6-*keto*-1 : 3-*dimethylpyridazine* distilled from a Widmer flask as a colourless liquid (6·44 g., 49·1%) of b. p. 142—143°/15 mm., $n^{21\cdot5}$ 1·4867 (Found : C, 57·5; H, 7·8; N, 22·6. $C_6H_{10}ON_2$ requires C, 57·1; H, 7·9; N, 22·2%).

Treatment of 1 : 4 : 5 : 6-*Tetrahydro*-6-*keto*-1 : 3-*dimethylpyridazine with Bromine.*—A solution of the ketone (0·94 g.) in glacial acetic acid (10 c.c.) was warmed and bromine (2·38 g.) slowly added; hydrogen bromide was evolved. The solution was allowed to cool and then evaporated to dryness. The solid residue recrystallised from acetic acid–ether formed colourless needles (0·67 g., 43·7%), m. p. 150° alone or on admixture with 1 : 3-dimethyl-6-pyridazone monohydrobromide (Found : C, 35·0; H, 4·5. Calc. for $C_6H_8ON_2$,HBr : C, 35·1; H, 4·4%). The product (0·47 g.) was dissolved in water (7·5 c.c.) and the solution warmed for 15 minutes. After cooling it was neutralised with barium carbonate and filtered. The filtrate was extracted with benzene and the extract dried ($MgSO_4$). After removal of the solvent, the liquid residue was distilled under diminished pressure. The distillate (0·13 g., 64%) solidified on cooling to a white solid of m. p. 50° alone or in admixture with 1 : 3-dimethyl-6-pyridazone (Found : C, 57·7; H, 6·1; N, 23·0. Calc. for $C_6H_8ON_2$: C, 58·1; H, 6·4; N, 22·6%).

Condensation of Ethyl β-Acetylacrylate with Methylhydrazine.—Ethyl β-acetylacrylate (see below) (5·4 g.) was added to a solution of methylhydrazine sulphate (5·4 g.) in aqueous sodium hydroxide (1 mol., 3 g.). Sufficient alcohol was added to make the mixture homogeneous, and the solution boiled under reflux for 1 hour. It was then filtered and the filtrate evaporated to dryness. The residue was made alkaline with sodium hydroxide and extracted with benzene. The extract was dried ($MgSO_4$) and evaporated to an oil which crystallised. It was 1 : 3-dimethyl-6-pyridazone (0·8 g., 17%) and showed m. p. 50° alone or on admixture with an authentic specimen.

Acetylation of 1 : 4 : 5 : 6-*Tetrahydro*-6-*keto*-3-*methylpyridazine.*—Anhydrous ketone (2·48 g.), fused and powdered sodium acetate, and acetic anhydride (20 c.c.) were boiled together under reflux for 0·5 hour. The mixture was allowed to cool and poured into water. The solution was neutralised with sodium hydrogen carbonate and extracted with chloroform, the extract dried ($MgSO_4$), and the solvent removed by distillation. The syrupy residue distilled as a colourless oil (1·72 g.) at 160° (bath-temp.)/0·005 mm. and showed $n^{20·5}$ 1·5084. This was probably 1 : 2-diacetyltetrahydro-3-keto-6-methylpyridazine (Found : C, 55·2; H, 6·6. Calc. for $C_9H_{12}O_3N_2$: C, 55·1; H, 6·2%). It showed no selective absorption in the ultra-violet above λ 2300 A. (*c*, 22·6 mg. % in water or dilute alkali).

Treatment of 1 : 4 : 5 : 6-*Tetrahydro*-6-*keto*-3-*methylpyridazine with Diazomethane.*—1 : 4 : 5 : 6-Tetrahydro-6-keto-3-methylpyridazine monohydrate (12 g.) was dehydrated by heating it at 100° under diminished pressure for 4 hours. It was dissolved in dry methyl alcohol (50 c.c.), the solution cooled to 0°, diazomethane (1 mol.) in ether added, and the mixture kept overnight. No reaction occurred. On evaporation of the solvents unchanged ketone monohydrate, m. p. 82°, was recovered in quantitative yield, after recrystallisation from water.

3-*Methylpyridazine.*—(*a*) 3-Chloro-6-methylpyridazine (2·22 g.), red phosphorus (1·11 g.), and hydriodic acid (11·1 c.c.) were intimately mixed and the mixture boiled under reflux for 1·25 hours. Hot water was added and the mixture was filtered with charcoal. The filtrate was evaporated to dryness, aqueous potassium hydroxide added until the mixture was alkaline, and the solution extracted with ether. After removal of the ether, 3-methylpyridazine distilled as a pale yellow liquid (1·02 g., 63%), b. p. 214° (decomp.), 190° (bath-temp.)/15 mm. Decomposition was reduced by distillation in an atmosphere of nitrogen.

(*b*) 3-Chloro-6-methylpyridazine (1·82 g.) was dissolved in absolute alcohol (20 c.c.) and hydrogenated at room temperature over a Raney nickel catalyst (32 c.c. of hydrogen were absorbed at N.T.P.). Thereafter the solution was filtered and evaporated to dryness. The presence of ionised chlorine was confirmed in the residue. To this, excess of aqueous potassium hydroxide was added. An oil separated which was extracted with ether. The extract was dried ($MgSO_4$) and filtered and the solvent evaporated off. Ether was added to the semi-solid product and the mixture filtered. The ether-insoluble residue recrystallised from light petroleum in colourless needles (1·2 g.), m. p. 58° alone or on admixture with 3-chloro-6-methylpyridazine. The ethereal extract was evaporated to dryness and the residue of 3-methylpyridazine, distilled, forming a colourless liquid (0·35 g.), b. p. 214°, darkening on exposure to light. Some of the distillate (0·1 g.) was dissolved in absolute ethyl alcohol, and dry hydrogen chloride was bubbled through the solution. Solid 3-*methylpyridazine monohydrochloride* separated which, after recrystallisation from alcohol–ether, had m. p. 184° (Found : C, 45·9; H, 5·5; Cl, 26·8. $C_5H_6N_2$,HCl requires C, 45·9; H, 5·3; Cl, 27·2%).

β-Bromolævulic Acid.—A solution of lævulic acid (40 g.) in concentrated hydrochloric acid (*d* 1·16; 140 c.c.) was cooled to 0° and bromine (17·2 c.c.) slowly added with stirring during 3 hours. Thereafter the solution was poured into water (700 c.c.), filtered from a small amount of βδ-dibromolævulic acid (m. p. 114°), and then extracted with ether. The ethereal extract was dried ($MgSO_4$) and the solvent removed by distillation. The yellow syrup could not be induced to crystallise and distilled as a very pale yellow liquid at 180°/0·02 mm.; it had n^{19} 1·4842. On cooling, the distillate crystallised and formed fine white needles, m. p. 53°, from carbon disulphide. The residue in the distillation flask, recrystallised from light petroleum, formed white needles, m. p. 114°, and was βδ-dibromolævulic acid. When the experiment was carried out at higher temperatures somewhat greater yields of βδ-dibromolævulic acid were obtained. The results are summarised in the following table.

Temp. of bromination	0°	19°	25°	30°
β-Bromolævulic acid, %	83	82	76	75
Dibromolævulic acid, %	5·0	6·0	10·0	12·3

β-Chlorolævulic Acid.—Chlorine was bubbled through a solution of lævulic acid (19·31 g.) in concentrated hydrochloric acid (*d* 1·16; 66·6 c.c.) at 0° until the theoretical gain in weight (6 g.) had taken place. The solution was then poured into water, the aqueous solution extracted with ether, and the ethereal extract dried ($MgSO_4$). After removal of the solvent a light yellow oil remained. This was distilled and collected in two fractions : a pale straw coloured oil (20 g., 79·4%), b. p. 123·5—127°/0·045 mm.,

n^{20} 1·4583, β-chlorolævulic acid; and a colourless syrup (1·9 g., 9·1%), b. p. 150°/0·045 mm., n^{20} 1·4698, which crystallised and had m. p. 77° alone or on admixture with βδ-dichlorolævulic acid (cf. Seissl, *Annalen*, 1888, **249**, 290).

β-Acetylacrylic Acid.—(*a*) β-Bromolævulic acid (112·8 g.), freshly fused and powdered sodium acetate (50 g.), and glacial acetic acid (250 c.c.) were boiled together under reflux for 1 hour. The solution was poured into water (1 l.) and the whole evaporated to dryness. The residue was acidified with hydrochloric acid and extracted with ether. The extract was dried ($MgSO_4$) and the solvent removed. The syrupy residue crystallised and, recrystallised from light petroleum, formed colourless needles of β-acetylacrylic acid m. p. 125—126° (56·9 g., 86%).

(*b*) β-Bromolævulic acid (9·23 g.) was boiled with water (50 c.c.) for 1 hour. Aqueous silver nitrate was added and the silver bromide removed by filtration. The filtrate was extracted with ether, the extract dried ($CaCl_2$), and the solvent evaporated. The resulting semicrystalline mass, after being pressed on porous tile and recrystallised from light petroleum, had m. p. 126° alone or on admixture with authentic β-acetylacrylic acid.

(*c*) β-Chlorolævulic acid (12·23 g.), freshly fused and powdered sodium acetate (12·23 g.), and glacial acetic acid (17·3 c.c.) were heated together at 100° for 40 minutes and the product was poured into water (150 c.c.). Acetylacrylic acid (6·22 g., 67·2%) isolated as above was obtained as colourless needles, m. p. 126°.

Ethyl β-Bromolævulate.—Ethyl lævulate (58·33 g.) in ether (100 c.c.) was cooled to 0° and bromine (10·5 c.c.) added dropwise during 3 hours with stirring. The pale yellow liquid was washed with water (4 times) and dried ($MgSO_4$). Evaporation of the ether gave ethyl β-bromolævulate (58·7 g., 65%) as a pale yellow syrupy liquid. This was used without further purification.

Ethyl β-Acetylacrylate.—(*a*) This was prepared in poor yield (24%) from β-acetylacrylic acid according to the method of Wolff (*Annalen*, 1891, **264**, 247) and was obtained as a colourless liquid which became red on storage; it showed b. p. 200—205°/760 mm., 110°/0·10 mm. The yield could be much improved (to 70%) by distilling the substance in the presence of quinol.

(*b*) Ethyl β-bromolævulate (58·7 g.), fused sodium acetate (21·6 g.), and glacial acetic acid (15·8 g.) were heated together at 100° for 30 minutes. On pouring the product into water a red oil separated. This was washed with dilute aqueous sodium carbonate and extracted with ether. The extract was dried ($MgSO_4$) and the solvent removed by evaporation. Ethyl β-acetylacrylate (22 g., 70%) was obtained as a pale yellow liquid, b. p. 110°/0·1 mm., after being distilled in the presence of quinol (0·5 g.) (phenylhydrazone, m. p. 116—117°). Wolff (*loc. cit.*) quotes b. p. 206° for this compound and described it as a red oil.

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