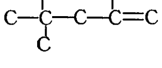
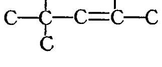
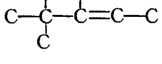
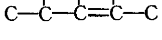
NOTES.

Note on the Intensity of the Double-bond Valence Vibration in Octenes. By T. A. Kletz and A. Sumner.

We have found the rules given by Thompson in his paper on the terpenes (this vol., p. 1412; *Proc. Roy. Soc.*, 1945, **184**, *A*, 13) for distinguishing different types of olefins by the frequency of the C–H deformation vibration at about 900 cm.$^{-1}$ very useful in identifying the octenes present in some samples of butene dimer. In the course of this work it was noted that the intensity of the band at about 1650 cm.$^{-1}$ due to the C=C valence vibration varies markedly between the different olefins, as summarised below.

Name.	Skeleton formula.	Strength (optical density of 0·1 mm. thickness).
2 : 4 : 4-Trimethylpent-1-ene	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{-}\overset{C}{C}{=}C}$	1
2 : 4 : 4-Trimethylpent-2-ene	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}C{=}\overset{C}{C}{-}C}$	0·35
3 : 4 : 4-Trimethylpent-2-ene	 $\mathrm{C{-}\overset{C}{\underset{C}{C}}{-}\overset{C}{C}{=}C{-}C}$	0·35
2 : 3 : 4-Trimethylpent-2-ene	 $\mathrm{C{-}\overset{C}{C}{-}\overset{C}{C}{=}\overset{C}{C}{-}C}$	0·14

It is clear that the strength of the band decreases with increase in the symmetry of the substitution about the double bond. This is presumably due to a decrease in the bond dipole moment accompanying the increase in symmetry.

The samples of these octenes, arranged above in order of boiling point, may be contaminated by small amounts of the adjacent members of the series. However, this would make the ratio of the densities of the first and the last member less than it should be, so that the true differences may be even greater than those shown in the table.—Research Department, Imperial Chemical Industries Ltd., Billingham Division. [*Received, February* 11*th*, 1948.]

Notes on the Formylation of Amines with Ethyl Formate. By J. P. E. Human and John A. Mills.

During researches with menthylamines it was found that crude (—)-menthylamine was best purified as its crystalline *N*-formyl derivative, and that the formyl derivative was very conveniently prepared by heating menthylamine with ethyl formate at 100—120°. The impure (—)-*N*-formomenthylamide made in this way was easier to purify than that made by formylation with formic acid. Hofmann (*Jahresber.*, 1865, 410) and Cosiner (*Ber.*, 1881, **14**, 58) have respectively formylated aniline and β-naphthylamine by reaction with ethyl formate, but the action on amines in general has not been studied before. We have found formylation of amines with ethyl formate to be of a general preparative value, unlike acylation with esters of higher fatty acids, which usually react slowly with all except the simplest amines, and being a formylation with a non-acidic reagent, several applications suggested themselves. Attention was directed particularly to the menthylamines and other *cyclo*hexylamines, because their higher acyl derivatives are difficult to hydrolyse, whereas the formyl derivatives are readily decomposed by refluxing with 5N-hydrochloric acid.

All primary amines tested (menthylamine, *neo*menthylamine, aniline, β-naphthylamine, 1-phenylethylamine) gave nearly quantitative yields of N-formyl derivative when heated with ethyl formate (10 mols.) at 100—110° for 1 hour. With a steel pressure vessel available, large quantities of amine could be formylated quickly, and the product was easily recovered by distillation of the excess ethyl formate. Small batches were safely done in sealed glass tubes, as the calculated pressure did not exceed 6 atmospheres. Under conditions comparable to the above, ethyl acetate did not react with menthylamine.

Of three secondary amines investigated, piperidine was completely formylated at 110°, but methylaniline and diphenylamine not at all. After 4 hours at 175° with ethyl formate (10 mols.), methylaniline was completely formylated, and diphenylamine about 25%. In many cases, by choosing suitable temperatures and reaction times, it should be possible to separate primary amines from secondary and tertiary, obtaining the free primary amines after an easy hydrolysis.

Cosiner (*loc. cit.*) formylated β-naphthylamine in unspecified yield by simple refluxing with ethyl formate in alcohol solution, but the temperature attained by this method was too low to give a sufficiently rapid reaction with less reactive amines. (—)-Menthylamine showed only 52% formylation after refluxing it with ethyl formate (5 mols.) in absolute alcohol (18 mols.) for 5 hours (internal temperature 68°).

The higher alkyl formates enable higher temperatures to be reached by refluxing, but the reaction is slower, and the working up less convenient. Menthylamine was refluxed for 1 hour with 10-molar quantities of *n*-butyl formate (b. p. 107°) and of *iso*amyl formate (b. p. 124°), giving 22% and 76% formylation respectively.

It seems to be possible to formylate primary amino-groups with ethyl formate and leave accompanying hydroxyl groups unaffected. When a mixture of menthylamine (1 mol.) and *cyclo*hexanol (1 mol.) was heated with ethyl formate (10 mols.) at 100° for 1 hour, and the product worked up by distillation under reduced pressure, the menthylamine was found to be completely formylated, whereas the recovered *cyclo*hexanol contained only 8% *cyclo*hexyl formate (by saponification value).

Attempts were made to use ethyl formate as the solvent in the catalytic hydrogenation of oximes and nitriles, because it seemed possible that the ester would formylate the primary amine as soon as it was formed, and so suppress the formation of secondary amine, which results from a reaction between primary amine and intermediate imine (Winans and Adkins, *J. Amer. Chem. Soc.*, 1932, **54**, 306). The results were unsatisfactory. With (—)-menthoxime and Raney nickel in ethyl formate, with or without the addition of pyridine, hydrogenation soon stopped, and nickel was found in the solution. Benzonitrile was hydrogenated easily at 100° over Raney nickel in ethyl formate containing a small quantity of pyridine, and the benzylamine was isolated as *N*-benzylformamide, but the melting point of this was low (35—45° instead of 49°), and on hydrolysis it gave benzylamine containing about 10% dibenzylamine.—Johnson Chemical Laboratories, University of Adelaide, Australia. [*Received, October* 13*th*, 1947.]

A Preparation of Lepidine. By D. Ll. Hammick and B. H. Thewlis.

The most recent reference to the laboratory preparation of lepidine is that of Neumann, Sommer, Kaslow, and Shriner (*Org. Synth.*, 1946, **26**, 45), in which 2-hydroxylepidine (4-methylcarbostyril) is first converted into 2-chlorolepidine, which is then catalytically reduced to lepidine. We have devised a simple method for the reduction of 2-hydroxylepidine direct to lepidine by the action of iodine and phosphorus in boiling xylene, in yields of 48·6%.

Experimental.—2-Hydroxylepidine (20 g., 1 mol., prepared by the method of Lauer and Kaslow, *Org. Synth.*, 1944, **24**, 68) was dissolved in xylene (400 ml.), and treated with red phosphorus (4 g., 1 g.-atom) and iodine (48 g., 3 g.-atoms); the mixture was boiled under reflux for 4 hours. Concentrated hydrochloric acid (100 ml.) was then added, and the xylene removed by steam distillation, after which the liquid was made alkaline with sodium hydroxide and the lepidine separated by distillation in steam.

The distillate was twice extracted with ether, the ethereal extracts being combined and dried (Na_2SO_4). The ether was removed, and the residue fractionated under reduced pressure, lepidine being collected at 135—137°/18 mm. Yield, 8·8 g. in each of three preparations (48·6% based on the 2-hydroxylepidine used). It formed a picrate, m. p. 212° (uncorr.); Campbell and Shaffner (*J. Amer. Chem. Soc.*, 1945, **67**, 86) give m. p. 212°.—THE DYSON PERRINS LABORATORY, OXFORD. [*Received, October* 21*st*, 1947.]

A Convenient Laboratory Preparation of Anhydrous Hydrazine. By H. J. BARBER and W. R. WRAGG.

THERMAL dissociation of the anhydrous phthalylhydrazide salt of hydrazine (Barber and Wragg, *J.*, 1947, 1332; B.P. Appl. No. 27900/46) in a simple evacuated apparatus gives anhydrous hydrazine in over 90% yield. This new method is more convenient than those dependent on the dehydration of high-strength hydrazine hydrate by distillation from barium oxide (Hale and Shetterly, *J. Amer. Chem. Soc.*, 1911, **33**, 1071) or sodium hydroxide (Smith and Howard, *Org. Synth.*, **24**, 53), particularly in that relatively dilute hydrazine hydrate may be used as starting material. Furthermore, the salt is suitable for storage. It is best prepared from phthalimide or phthalylhydrazide; the method of Curtius and Foersterling (*J. pr. Chem.*, 1895, **51**, 371) using phthalic anhydride, in our hands, gave poor yields and products with low hydrazine content.

The hydrazine content of the salt has been determined by decomposing it with concentrated hydrochloric acid, filtering from the phthalylhydrazide (which interferes with the subsequent titration), and titrating the hydrazine in the filtrate by the iodate method of Kolthoff (*J. Amer. Chem. Soc.*, 1924, **46**, 2009). This procedure gives values in agreement with those calculated from Dumas determinations for nitrogen, but it should not be considered a precise analysis.

Phthalylhydrazide Salt of Hydrazine.—(a) *From phthalimide.* Hydrazine hydrate (25 c.c. of a 50%w/v aqueous solution; 2·5 mols.) was added to a suspension of phthalimide (14·7 g.) in boiling alcohol (178 c.c.). After 6 hours' refluxing, the white bulky product was collected at 0° and washed with alcohol. The anhydrous salt (17·5 g.; 90%) was obtained by drying this material over potassium hydroxide at 25°/25 mm. [Found: N, 28·6; N_2H_4 (by titration), 16·4. Calc. for $N_2H_4,C_8H_6O_2N_2$: N, 28·85; N_2H_4, 16·5%].

(b) *From phthalylhydrazide.* Phthalylhydrazide (48·6 g.) was dissolved at 90° in aqueous hydrazine hydrate (292 c.c. of a 16% w/v solution; 3·1 mols.). The solution was filtered and stirred into alcohol (800 c.c.). The white bulky precipitated salt was collected at 0°, washed with alcohol, and dried over potassium hydroxide at 25°/25 mm., giving 43 g. (74%), m. p. 340—344° (Found: N, 28·8%).

Determination of Hydrazine in the Salt.—An accurately weighed quantity (*ca.* 0·2 g.) of the phthalylhydrazide salt of hydrazine was stirred at room temperature with concentrated hydrochloric acid (25 c.c.) for 30 minutes. The suspension obtained was filtered on a sintered glass funnel and the residue washed with concentrated hydrochloric acid (5 c.c.) followed by water (20 c.c.). The hydrazine content of the combined filtrate was determined by the iodate method of Kolthoff (*loc. cit.*).

Anhydrous Hydrazine.—The apparatus used consisted of an all-glass distillation flask, immersed in a heating bath and sealed to a U-shaped receiver which was connected to an oil pump. There were constrictions in the two limbs of the receiver at which it could be sealed off and removed while still evacuated. Finely powdered anhydrous phthalylhydrazide salt of hydrazine (9·7 g.) was filled into the flask and covered with a plug of glass wool. The apparatus was evacuated to 0·01 mm. and the receiver placed in a solid carbon dioxide–acetone bath. The temperature of the salt was raised slowly to 180°, by which time the anhydrous hydrazine had collected as a practically colourless solid, 1·47 g. [92%; 99·5% pure by iodate method of Kolthoff (*loc. cit.*)]. The product solidified completely when the sealed-off receiver was placed in ice–water (hydrazine has m. p. 1·4°).

We are indebted to Mr. S. Bance, B.Sc., A.R.I.C., for the semimicro-analyses and to the Directors of May and Baker Ltd. for permission to publish these results.—RESEARCH LABORATORIES, MAY AND BAKER LTD., DAGENHAM, ESSEX. [*Received, October* 21*st*, 1947.]

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1 : 1 : 1-*Trichloro*-2 : 2-*di*-(p-*aminophenyl*)*ethane.* By I. E. BALABAN and M. B. LEVY.

We have prepared over a period of years many substituted diaminodiphenyltrichloroethanes by the well-known method of nitration, followed by reduction of the resulting nitro-compound, employing stannous chloride in hydrochloric acid solution. On repeating this procedure with 1 : 1 : 1-trichloro-2 : 2-diphenylethane, the amino-compound (I; $R = NH_2$) did not correspond with that prepared by Kirkwood and Phillips (*J. Amer. Chem. Soc.*, 1946, **68**, 2405), whose method differed in that the reduction was carried out catalytically. Our compound gave good analyses for all four elements, whereas Kirkwood and Phillips gave only a nitrogen figure. Furthermore, we obtained the constitution of (I; $R = NH_2$) by benzoylation to (I; $R = NHBz$), dehydrochlorination to (II; $R = NHBz$), and oxidation to 4 : 4′-*dibenzamidobenzophenone* (III; $R = NHBz$), the last being also prepared from 4 : 4′-diaminobenzophenone (III; $R = NH_2$).

$$\underset{\text{(I.)}}{CCl_3{\cdot}CH(C_6H_4R)_2} \qquad \underset{\text{(II).}}{CCl_2{:}C(C_6H_4R)_2} \qquad \underset{\text{(III.)}}{CO(C_6H_4R)_2} \qquad \underset{\text{(IV.)}}{CCl_3{\cdot}CH(OH){\cdot}C_6H_4{\cdot}NH_2}$$

Several years earlier a study had also been made of the condensation of acetanilide with chloral in the presence of concentrated sulphuric acid, but hydrolysis of the resulting condensation product yielded only 2 : 2 : 2-*trichloro*-1-(p-*aminophenyl*)*ethanol* (IV). Burger, Graef, and Bailey (*J. Amer. Chem. Soc.*, 1946, **68**, 1725), however, carried out the condensation of dibenzanilide with chloral in the presence of concentrated sulphuric acid and claimed that mild hydrolysis of the reaction product yielded 1 : 1 : 1-trichloro-2 : 2-di-(*p*-benzamidophenyl)ethane. The latter compound did not correspond to that obtained by direct benzoylation of the amine prepared by us, but repetition of the American authors' work showed that their substance could be further purified by recrystallisation from acetic acid to give the same benzoylated amine. [As our investigation was nearing completion, Kirkwood and Phillips (*ibid.*, 1947, **69**, 934) completely substantiated our own results.]

Experimental. (All m. p.s are uncorrected.)—1 : 1 : 1-*Trichloro*-2 : 2-*di*-(p-*aminophenyl*)*ethane* (I; R = NH_2). 1 : 1 : 1-Trichloro-2 : 2-di-(*p*-nitrophenyl)ethane (7·5 g.) was suspended in boiling ethanol (100 ml.) and a solution of stannous chloride (29 g.) in concentrated hydrochloric acid (32 ml.) was added slowly during ½ hour. After a further hour's refluxing, the mixture was cooled and then poured on a mixture of ice and sodium hydroxide solution so that the mixture remained alkaline. The solid was collected, washed, with water, and reprecipitated from dilute hydrochloric acid solution by sodium hydrogen carbonate. It recrystallised from ethanol in pale yellow needles (4·3 g., 68%), m. p. 148—149° (Found: C, 52·3; H, 4·3; N, 8·5; Cl, 33·8. Calc. for $C_{14}H_{13}N_2Cl_3$: C, 53·3; H, 4·15; N, 8·9; Cl, 33·7%). Kirkwood and Phillips gave m. p. 154—155°.

The dibenzamido-derivative had m. p. 234—238° (Found: C, 63·6; H, 4·2; N, 5·25; Cl, 20·6. Calc. for $C_{18}H_{21}O_2N_2Cl_3$: C, 64·2; H, 4·0; N, 5·35; Cl, 20·4%). Burger, Graef, and Bailey (*loc. cit.*) gave m. p. 165—168°, and the product prepared by their method, on recrystallisation from glacial acetic acid, had m. p. 232—235°, and gave no depression on admixture with the compound as prepared above.

1 : 1-*Dichloro*-2 : 2-*di*-(p-*aminophenyl*)*ethylene* (II; R = NH_2). This was prepared by the action of ethanolic potassium hydroxide on (I; R = NH_2) and had m. p. 139—140° (Kirkwood and Phillips gave m. p. 144—145°) (Found: C, 59·6; H, 4·6; N, 10·4; Cl, 25·8. Calc. for $C_{14}H_{12}N_2Cl_2$: C, 60·25; H, 4·3; N, 10·05; Cl, 25·4%). The same compound was also obtained as follows: 1 : 1-Dichloro-2 : 2-di-(*p*-nitrophenyl)ethylene (1·0 g.) was dissolved in boiling methanol and a solution of stannous chloride (4·9 g.) in concentrated hydrochloric acid (5·5 ml.) was added during 15 minutes. Boiling was continued for 1 hour, and the product was worked up as for (I; R = NH_2) and recrystallised from benzene, forming light yellow needles, m. p. 139—140°; yield 0·4 g., 49%. A mixed m. p. with a sample prepared by hydrolysis of the amino-compound (I; R = NH_2) showed no depression.

1 : 1-*Dichloro*-2 : 2-*di*-(p-*nitrophenyl*)*ethylene* (II; R = NO_2) (Lange and Zufall, *Annalen.*, 1893, **271**, 2). This was also prepared from the corresponding ethane with methanolic potassium hydroxide and had m. p. 171—172°.

4 : 4′-*Dinitrobenzophenone* (III; R = NO_2). 1·5 G. of (II; R = NO_2) were dissolved in glacial acetic acid (30 ml.), and chromium trioxide (5·0 g.) added at room temperature during 2 hours. The mixture was then refluxed for 4 hours, cooled, and poured into water; the solid which separated was collected, washed, dried, and recrystallised from ethanol, giving colourless platelets (1·1 g.), m. p. 187—188°.

4 : 4′-*Diaminobenzophenone* (III; R = NH_2). This was prepared according to Biltz (*Annalen*, 1897, **296**, 226) and had m. p. 235—237°. Biltz gave m. p. 244° (corr.).

1 : 1-*Dichloro*-2 : 2-*di*-(p-*benzamidophenyl*)*ethylene* (II; R = NHBz). This was prepared from (I; R = NHBz) by heating with methanolic potassium hydroxide and had m. p. 255—260°.

4 : 4′-*Dibenzamidobenzophenone* (III; R = NHBz). 0·75 G. of (II; R = NHBz) was suspended in glacial acetic acid (15 ml.) and chromium trioxide (2·5 g.) was added at room temperature during 1½ hours, the solid dissolving. The solution was then treated as for (III; R = NO_2), and crystallisation of the solid from methanol and then from ethanol afforded colourless needles (0·35 g., 54%), m. p. 225—228°. This *compound* was also prepared by benzoylation of 4 : 4′-diaminobenzophenone and a mixed m. p. showed no depression (Found: C, 77·2; H, 5·0; N, 7·2. $C_{27}H_{20}O_3N_2$ requires C, 77·15; H, 4·8; N, 6·7%). Burger, Graef, and Bailey (*loc. cit.*) prepared this compound (m. p. 151—152°) from 1 : 1 : 1-trichloro-2 : 2-di-(*p*-benzamidophenyl)ethane, m. p. 165—168°. Its constitution was stated to be established by identity with a synthetic product (only nitrogen determination given) prepared from benzanilide and carbon tetrachloride (use of anhydrous aluminium chloride).

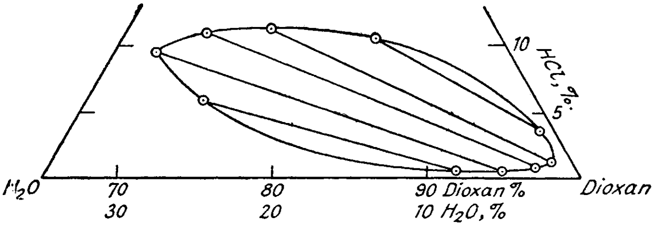
2 : 2 : 2-*Trichloro*-1-(p-*acetamidophenyl*)*ethanol.* To a mixture of acetanilide (270 g.) and chloral (148 g.), concentrated sulphuric acid (1 l.) was added slowly (2 hours) with cooling and occasional shaking. After each addition, the temperature tends to rise and solution takes place. After four days with occasional shaking, the mixture was poured on ice (2 kg.), and the product was washed with water (6—8 l.), then with saturated sodium carbonate solution, and finally with water to neutrality. A thick plastic mass resulted; this was kept overnight with glacial acetic acid (200 ml.), and next day it was stirred and a solid separated. This was collected and washed with 2 N-acetic acid, and then had m. p. 209°, raised by recrystallisation from aqueous alcohol to 212° (decomp.) (yield 25 g.). Burger, Graef, and Bailey gave m. p. 211—213° (decomp.).

2 : 2 : 2-*Trichloro*-1-(p-*aminophenyl*)*ethanol* (IV). The above acetyl derivative (20·9 g.) was heated under reflux with hydrochloric acid (16%; 150 ml.) for one hour, complete solution being obtained. This was filtered (charcoal) and basified with 30% sodium hydroxide solution and finally with soda ash; a thick tar was obtained which on agitation and keeping for 24 hours solidified. This material. (15 g., m. p. 70—80°) was insoluble in water but readily soluble in 95% alcohol. It was dried and extracted with benzene which left an insoluble tar. The benzene solution was concentrated to low volume, and light petroleum (b. p. 60—80°) added; the resulting *substance* had m. p. *ca.* 102°, and two recrystallisations from chloroform (charcoal) afforded almost colourless thick prisms (4·9 g.), m. p. 112—113° (Found: N, 5·9; Cl, 44·35. $C_8H_8ONCl_3$ requires N, 5·8; Cl, 44·3%).

All analyses were by Drs. Weiler and Strauss.—PHARMACEUTICAL LABORATORY, THE GEIGY COMPANY LTD., TRAFFORD PARK, MANCHESTER, 17. [*Received, October 28th,* 1947.]

The System Hydrogen Chloride–Dioxan–Water at 25°. By R. A. Robinson and R. C. Selkirk.

Although it has long been known that this system can separate into two liquid layers, the conditions for the existence of two liquid phases do not seem to have been studied quantitatively. We have investigated this system at 25° by shaking the components together in sealed containers for 3 hours and then analysing each layer for (*a*) hydrogen chloride by direct titration, and (*b*) water by neutralising with excess of sodium carbonate, distilling to dryness, and determining the refractive index of the distillate. Separate refractive-index measurements were made on synthetic dioxan–water mixtures from which a graph of refractive index of the mixture against the water content was constructed. These measurements were in good agreement with those of Hovorka, Schaefer, and Dreisbach (*J. Amer. Chem. Soc.*, 1936, **58**, 2264). The following results were obtained :



	Upper layer.			Lower layer.	
HCl, %.	H_2O, %.	$C_4H_8O_2$, %.	HCl, %.	H_2O, %.	$C_4H_8O_2$, %.
3·52	0·85	95·6	10·30	8·18	81·5
1·17	1·29	97·5	11·25	14·40	74·3
0·87	2·63	96·5	10·91	18·36	70·7
0·47	4·84	94·7	9·59	22·69	67·7
0·49	7·78	91·7	5·76	21·55	72·7

The results are plotted in the figure, from which it may be seen that water–dioxan solutions containing 68—99% of dioxan will separate into two liquid layers on the addition of sufficient hydrogen chloride.—University College, Auckland, New Zealand. [*Received, September* 2*nd*, 1947.]