

851. *Molecular Photoelectron Spectroscopy. Part II.*¹
A Summary of Ionization Potentials.

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250 Ionization potentials smaller than 21.21 eV derived from the photoelectron spectra of 48 compounds are tabulated. The bonding character of the orbital level concerned in each ionization process is indicated. The results for nitrogen dioxide, ethylene, benzene, and pyridine are discussed. Autoionization is shown to be absent or unimportant.

WE have described^{1,2} a new experimental approach to the measurement of molecular ionization potentials based on photoelectron spectroscopy. The electron energy spectra obtained were shown to lead directly to the arrangement of the occupied electronic energy levels. The spectra also showed effects due to vibration in the positive ion resulting from one-electron loss from each level in turn. From comparison of the results obtained for hydrogen and nitrogen with other experiments and with theoretical calculations on these molecules we conclude that in general there should be a single sharp peak in the electron energy spectrum associated with each ionization potential *only* in the event of complete lack of bonding character in the orbital from which electron ejection occurred. It also appears that the extent of any bonding (or antibonding) character can be inferred from the relative intensities of the series of peaks corresponding to increasing vibrational levels reached in the product ion since the ionization is subject to Franck-Condon control. Where the vibrational structure cannot be resolved the degree to which the electron energy peak is broadened to lower electron energies indicates the bonding character. In Part I

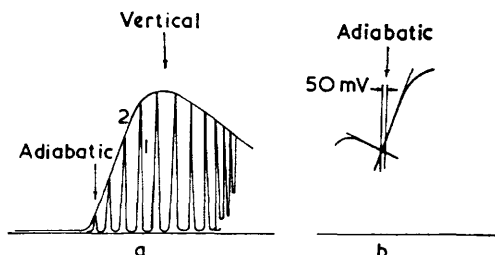
¹ Part I, Al-Joboury and Turner, *J.*, 1963, 5141.

² Turner and Al-Joboury, *J. Chem. Phys.*, 1962, **37**, 3007.

we showed that the highest electron energy peaks in such vibrational series provide ionization potentials in good agreement with the spectroscopically known adiabatic values for hydrogen and nitrogen. In the ground state of these molecules the excited vibrational levels are not appreciably populated at the temperature used. Herzberg gives for example for H_2 the population ratio for the $v(1)$ and $v(0)$ levels at $300^\circ K$ 2.16×10^{-9} and for O_2 5.74×10^{-4} .³ No peaks [e.g., $v(0) \leftarrow v(1)$] corresponding to ionization from the vibrationally excited electronic ground state were found. Such an effect has however been discussed by Watanabe⁴ and it can just be detected in the photoionization cross section curves for ammonia⁵ and nitric oxide.^{5,6}

Where the vibrational mode excited by electron removal (generally the stretching mode) is characterized by a quantum energy greater than about 0.1 eV and where it has

FIG. 1. A portion of a photoelectron spectrum (idealised) showing (a) the identification of adiabatic and vertical ionization potentials with resolved (1) and unresolved (2) vibrational structures, (b) the identification of a higher adiabatic ionization potential with a "break."



been resolved in the photoelectron energy spectrum no ambiguity about the derivation of the adiabatic ionization potentials arises (Fig. 1a; v in Table I). In the other, and more common, cases of unresolved vibrational (and probably rotational) fine structure selection of the point to be taken to represent adiabatic ionization is somewhat subjective. In addition, for small vibrational quanta appreciable population of excited vibrational levels in the molecule becomes possible; Herzberg gives for I_2 for example³ ($\nu = 213 \text{ cm}^{-1}$) the population ratio $v(1)/v(0)$ at $300^\circ K$ 0.36. It follows that when electron ejection occurs from orbitals involved in bonds having similar stretching frequencies errors of the order of 200 cm^{-1} or 0.04 eV may be introduced since $v'(0) \leftarrow v(1)$ ionizations will occur. As this is less than the energy resolution of the present apparatus we have assumed the latter to be the main source of imprecision. For consistency we have selected a value 50 mV (half the width at half height of the peaks obtained for the rare gases) to lower electron energies than the "break" in the electron energy spectrum (Fig. 1b) as representing adiabatic ionization.

Table I gives a summary of the proposed adiabatic ionization potentials derived from the photoelectron energy spectra of 48 compounds, a total of 250 potentials.

RESULTS AND DISCUSSION

In the simpler molecules listed (1—14, 21, 22, 23, 30) the individual electronic levels are well enough separated to be completely resolved in our spectra and an unambiguous total number of measurable ionization potentials (less than 21.21 eV) follows. In more complex molecules, in particular the saturated hydrocarbons and large alkyl group containing molecules we found considerable overlapping between the broad bands arising from closely spaced bonding levels with ionization potentials between 11 and 16 eV. The values given in such cases (in parentheses in Table I) relate to the more prominent "breaks" in the spectrum and though designated "dubious" are reproducible changes of slope and can

³ Herzberg, "Spectra of Diatomic Molecules," Van Nostrand, New York, 1950, p. 122.

⁴ Watanabe, *J. Chem. Phys.*, 1957, **26**, 542.

⁵ Watanabe, Nakagama, and Mottl, "Final Report on Ionization Potentials" (1959), U.S. Army Contract DA-04-200 ORD 482, 737.

⁶ Clouthier and Schiff, *J. Chem. Phys.*, 1939, **31**, 793.

TABLE I.

Proposed adiabatic ionization potentials (ev) derived from photoelectron energy spectra excited by 21.21 eV photons. Bonding character of orbital concerned: n.b., non-bonding; w, weakly bonding (or antibonding); v, weakly bonding (or antibonding); otherwise strongly bonding (or antibonding); v, vibrational structure. Dubious values in parentheses (see text).

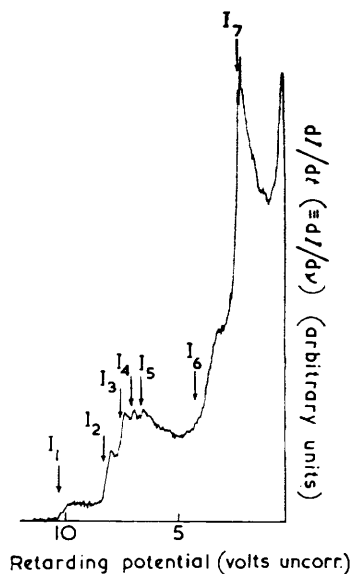
1	O ₂	1.07w, v	16.42v	17.99w, v	20.12w, v
2	CO	14.01 n.b.	16.51v	19.72w, v	18.27v
3	NO	9.34v	15.23	16.5 n.b.	
4	H ₂ O	12.61w, v	14.23	18.02	
5	D ₂ O	12.69w, v	14.28	18.07	
6	H ₂ S	10.42 n.b.	12.62	14.82	
7	Cs ₂	10.07 n.b.	12.62w	14.52 n.b.	18.42 (19.31)
8	SO ₂	12.32w	13.17	16.42w	16.82 (18.00)
9	NO ₂	10.97	12.82w	13.48w	16.17w (20.07)
10	N ₂ O	12.82 n.b.	(15.37)	16.37w	(14.37) 16.79 18.86w, v
11	CO ₂	13.68w	17.23	18.08w	20.10w, v
12	NH ₃	10.16	15.02		
13	Methane	12.99			
14	Ethane	11.49	14.74	(20.13)	(19.18)
15	Propane	11.07	13.17	15.17	15.70 (18.57)
16	n-Butane	10.50	12.36	14.13	(15.69) (19.96)
17	Isobutane	10.78	12.54	14.51	(18.63) (19.86)
18	n-Heptane	10.20	14.38	15.18	(18.63) (19.86)
19	2,2,4-Trimethylpentane	9.91	(11.95)	(14.09)	(19.74)
20	Cyclohexane	9.79	(11.33)	12.22	14.37 19.43
21	Acetylene	11.41w	16.41	18.56	(20.51)
22	Ethylene oxide	10.49w	11.48	13.48	16.16 (20.16)
23	Ethylene	10.48w	12.50	14.39	(19.13) 15.63 (18.78)
24	Butadiene	9.08w	11.25	12.14	13.23 15.14 (15.74)
25	Cyclohexene	8.72w	10.29	10.98	12.47 (16.25)
26	α -Pinene	8.07w	9.25	11.43	13.12 14.53 (18.57)
27	Cyclo-octatetraene	8.04	9.49	10.84	12.09 (15.74)
28	Benzene	9.25	11.49	(12.19)	13.67 14.49 (16.44)
29	Pyridine	9.28	10.54 n.b.	12.22	(13.43) 14.44 (17.69)
30	Methyl alcohol	10.83w	12.33	14.64	(19.82) 15.49 (19.39)
31	Ethyl alcohol	10.63w	11.81	12.80	15.69 (20.14)
32	Acetone	9.67w	12.16	(14.15)	17.38 20.12 (17.92)
33	Diethyl ether	9.61w	11.08	(11.92)	15.55 19.88 (19.67)
34	Methamine	9.18	12.16	(13.94)	16.57 (19.89)
35	Ethylamine	9.19	11.86	12.66	15.55 16.81 (19.09)
36	Isopropylamine	8.86	11.23	14.87	15.55 (19.35)
37	n-Butylamine	8.79	10.75	(14.11)	15.28 (19.46)
38	t-Butylamine	8.83	9.81	12.46	15.11 (19.62)
39	Cyclohexylamine	8.86	10.25	14.56	18.17 (19.62)
40	Dimethylamine	8.36	12.88	14.63	16.35 (19.18)
41	Diethylamine	8.51	11.08	14.45	(19.34)
42	Trimethylamine	8.12	11.63	13.52	(19.92) 15.31 18.62 (19.50)
43	Triethylamine	7.84	10.79	14.36	15.37 14.36 (19.02)
44	Pyrrolidene	8.41	11.10	14.13	16.64 15.16 (19.50)
45	CH ₃ CH ₂ NET	9.29	10.57	11.63	12.55 14.08 (19.17)
46	(CH ₃) ₂ C:NET	8.83	9.79	11.63	13.37 (19.17)
47	Pr-CH ₂ NET	9.00	10.15	11.15	13.28 (19.17)
48	(CH ₃) ₂ CHCH ₂ NET	8.94	10.12	11.08	12.64 (19.17)

thus attract a similar degree of confidence in their precision to mass spectrometric ionization potentials. The possibility is not excluded in these cases that other levels in the vicinity may be detected by refinements of the technique.

The detailed discussion of the form of the electron energy spectrum for each compound and the critical comparison of the ionization potentials and vibrational frequencies with spectroscopic and electron impact data where this is available is deferred to later Papers when isoelectronic and similarly related groups will be considered together. There are a few results, however, which deserve immediate comment.

Nitrogen Dioxide.—The first ionization potentials of di- and tri-atomic molecules are usually quite accurately known, with good agreement between different methods of measurement. Nitrogen dioxide (Fig. 2) is a notable exception with values for the first ionization potential ranging from 9.78 to 13.98 eV. Whilst the latter value may relate to a

FIG. 2. The photoelectron spectrum of nitrogen dioxide ($p = 0.014$ mm.). Electron energy increasing from right to left.



higher ionization potential it is difficult to separate the literature values into groups relating to different electronic levels since they are distributed with some uniformity. Collin⁷ in a recent survey concludes that only the lowest values obtained by photoionization (9.78 and 9.80 eV) and the indirect electron impact values (9.91, 9.93, 10.04 eV) relate to the first ionization potential (mean 9.89 eV). The photoionization yield curve⁸ (σ_i versus λ), *i.e.*, the only previous *direct* measurement, shows ionization down to 9.78 eV. It shows, however, a further rise at 10.83 eV identified with the process $\text{NO}_2 \rightarrow \text{NO}^+ + \text{O}^-$. Professor W. C. Price⁹ has pointed out however that neither of these assignments is necessarily true since the first value might be accounted for by an *increase* in the photoionization of nitric oxide following the onset of a dissociation process $\text{NO}_2 \rightarrow \text{NO} + \text{O}$ at 9.7–9.8 eV. The strong lines in the absorption spectrum near 1300 Å show marked broadening possibly due to predissociation. The second might be accounted for by an autoionization of NO_2 , since there is a strong, broad line in the spectrum of NO_2 at the same wavelength which appears to be the first member of a Rydberg series converging to a value a little greater than 11 eV. It seems likely, therefore, that our value of 10.97 is really the first direct measurement of the first ionization potential of NO_2 . Its appearance is consistent with

⁷ Collin, *Bull. Soc. Royale Sciences Liège*, 1963, 133.

⁸ Nakayama, Kitamura, and Watanabe, *J. Chem. Phys.*, 1959, 30, 1180.

⁹ Price, personal communication.

a strongly antibonding electron's being involved; the difference between the vertical and adiabatic ionization potential seems to lie between 0.5 and 1.0 v.

Benzene and Pyridine.—The first ionization potentials recorded here (Fig. 3a and b) are in good agreement with the spectroscopic values¹⁰⁻¹² (benzene, 9.24; pyridine, 9.26 ev) as also is the second ionization potential for benzene¹³ (11.49 ev). In benzene we find no intermediate values (*vide infra*) and the first two probably relate to the two occupied π levels (e_{2g} , b_{2g} , the first being doubly degenerate). The spacing between them, 2.25 ev, should be equal to β_0 and is in good agreement with other estimates of this parameter.¹² The nearest corresponding levels in pyridine have a separation of 2.94 ev. However, in pyridine an additional level is found just below the first and we assign this second ionization

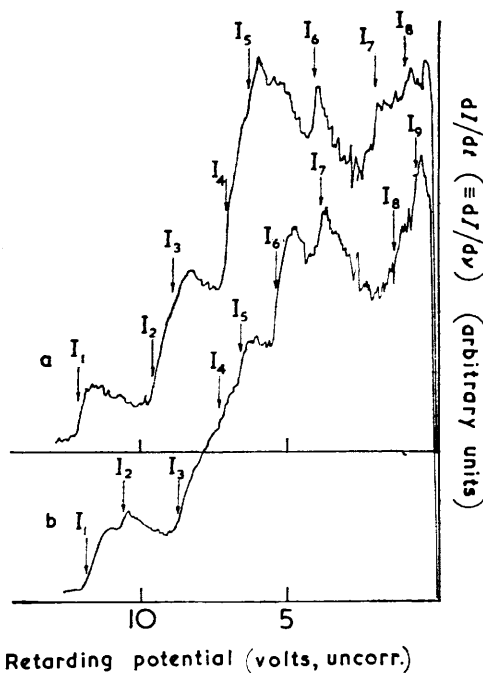


FIG. 3. The photoelectron spectra of benzene (a) and pyridine (b) ($p = 0.018$ and 0.022 mm., respectively).

potential (10.54 ev) to the nitrogen lone pair electrons on account of the appreciably lower bonding character which the shape of the peak suggests as compared with that of the highest level. The relative intensities of the peaks also support this assignment. El-Sayed and Kasha¹³ have reported some sharp strong lines in the pyridine absorption spectrum which appear to converge towards ~ 10.3 ev which we presume corresponds to our second ionization potential, and these lines El-Sayed and Kasha also tentatively associated with the lone pair electrons. One of our higher ionization potentials for benzene (11.39 ev), corresponding apparently to the deepest π level, also appears to have been observed by El-Sayed and Kasha (11.48 ev) and in addition their value of 16.84 ev probably refers to the same level as our value of 16.73 ev. There is, however, no counterpart in our spectrum to their 11.56 ev for the third ionization potential of pyridine.

Pyridine Charge-transfer Complexes.—Pyridine is somewhat exceptional in correlations of ionization potential with the energy of charge-transfer bands with iodine as acceptor.

¹⁰ Price and Wood, *J. Chem. Phys.*, 1935, **3**, 439.

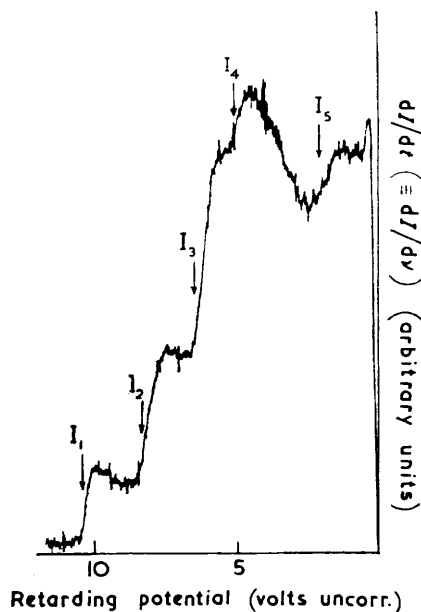
¹¹ Wilkinson, *J. Chem. Phys.*, 1956, **24**, 917.

¹² Cf. Streitwieser, "Molecular Orbital Theory for Organic Chemists," Wiley, New York, 1961, p. 186 ($\beta_0 = 2.05$ ev; polarographic reduction), 192 ($\beta_0 = 2.48, 3.14$ ev; ionization potentials), 201 ($\beta_0 = 2.0$ ev charge transfer complexes), 217 ($\beta_0 = 2.36$ ev; spectra).

¹³ El-Sayed and Kasha, *J. Chem. Phys.*, 1961, **34**, 334.

Extrapolation¹⁴ from the values for donors such as benzene, dioxan, and thio-ethers would lead to a value for pyridine greater than the observed first ionization potential. By analogy with benzene, the charge-transfer band was taken to involve the highest occupied π level leaving the first ionization potential to be assigned to the nitrogen lone pair electrons.

FIG. 4. The photoelectron spectrum of ethylene ($p = 0.03$ mm.).



Our measurement of the second ionization potential (10.54 eV) accords well with the view that in the pyridine-iodine complex, pyridine is donating electrons from the second highest orbital level (predicted I.P. ~ 10 eV) but the photoelectron spectrum indicated this to be the nitrogen lone pair orbital. This also accords better with the planar, centrosymmetric structure for the dipyridineiodine cation in the solid state.¹⁵

Ethylene.—An analogy has recently been drawn between the structures of ethylene and formaldehyde by R. S. Berry¹⁶ in an attempt to relate the low intensity “shoulder” which most olefins show on the long wavelength side of the $N \rightarrow V$ transition near 2000 Å to the $n \rightarrow \pi^*$ transition of the carbonyl grouping. Ethylene has been described in molecular orbital terms by Mulliken as:

$$\begin{array}{lll} \psi 1 (b, x + x)^2 & \psi 3 (b_2, y)^4 & \psi 5 (a, s + s)^2 \\ \psi 2 (a, \sigma + \sigma)^2 & \psi 4 (b, s - s)^2 & \end{array}$$

Our photoelectron spectrum (Fig. 4) is consistent with this order of energies since the first ionization potential is clearly associated with the least strongly bonding electrons, evidently $\pi_x(\psi 1)$, weakly C-C bonding in contrast to electrons in the other levels $\psi 2$ — $\psi 5$ all of which are strongly C-C or C-H bonding. Berry's treatment requires $\psi 3$ to be higher in energy than $\psi 1$ by about 1.5 eV, a relative order which on grounds of the probably higher bonding character of $\psi 3$ (strongly C-H bonding) appears inconsistent with our results. In addition the upper state of this has been shown by D. F. Evans,¹⁷ using the technique of pressure broadening, to be Rydberg in character; *i.e.*, to be *different* from the π^* upper state postulated by Berry.

¹⁴ Mason, *Physical Methods in Heterocyclic Chemistry*, ed. Katritzky, Vol. II, p. 77 (Academic Press, 1963).

¹⁵ Hassel and Hope, *Acta Chem. Scand.*, 1961, **15**, 407.

¹⁶ Berry, *J. Chem. Phys.*, 1963, **38**, 1934.

¹⁷ Evans, *Proc. Chem. Soc.*, 1963, 378.

There is no evidence in the spectrum of a second ionization potential as small as 11.74 eV (Table 2, ref. *f*), and this low value may possibly be ascribable to autoionization (*vide infra*). The separation between the first two ionization potentials (2.02 eV) is thus probably too great to allow us to take even the second level as ψ_3 for the purpose of accommodating an $n \rightarrow \pi^*$ like transition (cf. ref. 16, p. 1937).

Autoionization.—Ionization potential determination by threshold techniques, where the *critical* photon or electron energy required to produce a change in mode of ion production is varied may (as in the above examples) suggest more ionization potentials than there are occupied orbitals. Whilst there is generally good agreement between the higher ionization potentials reported here and such corresponding values as have been obtained by the alternative methods, some reported ionization potentials have no counterpart at all among the energy levels revealed by our spectra. Some of these anomalous values are recorded in Table 2. The value for benzene (10.46 eV) is recognized¹⁸ as due to auto-

TABLE 2.

Ionization potentials measured by electron impact or derived from photoionization cross-sections which are not observed by photoelectron spectroscopy.

Oxygen	16.97, 17.18 ^{a, b}
Nitrogen	19.4 ^a
Hydrogen sulphide	16.07 ^c
Carbon disulphide	12.01, 13.60 ^d
Water	16.97 ^e
Nitrous oxide	13.10, 13.60, 14.1 ^h
Nitrogen dioxide (see text)	9.78 (? 10.83) ^g
Acetylene	13.25 ^f
Ethylene (see text)	11.74 ^f
Methanol	18.85 ^e
Methylamine	17.2 ^e
Benzene (see text)	10.46 ¹⁶

References.—^a Clarke, *Canad. J. Phys.*, 1954, **32**, 764; ^b Frost and McDowell, *J. Amer. Chem. Soc.*, 1958, **80**, 10,183; ^c Frost and McDowell, *Canad. J. Chem.*, 1958, **36**, 39; ^d Collin, *J. Chim. phys.*, 1960, **57**, 416, 424; ^e Collin, *J. Chem. Phys.*, 1959, **30**, 1621; ^f Collin, *Bull. Soc. Chim. belges*, 1962, **71**, 15; ^g Collin, 9^e Colloquium Spectroscopium Internationale, Lyon, 1961, 596; ^h Curran and Fox, *J. Chem. Phys.*, 1961, **34**, 1590.

ionization from the second Rydberg band in the series going to the second ionization potential. Since we are concerned only with the consequences of the absorption of photons of fixed energy (21.21 eV), no peaks can arise in our spectra from autoionization initiated by transitions between levels whose difference is other than 21.21 eV. In addition, should a transition be excited by the 21.21 eV quanta and lead to autoionization, just the same groups of electron energies would be produced as from the initial direct photoionization though possibly with different relative probabilities and angular distribution of the ejected electrons, random directions probably occurring. We tentatively suggest, therefore, that comparison of the energy levels derived from mass spectrometric or photoion current yield curves with the photoelectron energy spectrum can reveal by their absence in the latter the autoionization-derived ones.

EXPERIMENTAL

The photoelectron spectrometer was described in Part I.¹

Materials.—All the condensable compounds were subjected to several cycles of evacuation whilst frozen (solid carbon dioxide or liquid nitrogen coolant) and thawing whilst isolated from the pumps in order to remove the more volatile impurities.

The following gases were from cylinders, purified only by fractional condensation: oxygen, carbon monoxide, carbon dioxide, nitric oxide, nitrous oxide, methane, ethane, and propane.

Nitrogen dioxide. This was prepared from lead nitrate according to the method of Cottrel

¹⁸ Cf. contributions by Momigny and Price, *Proceedings, Colloquium on Gaseous Ionization, Liège*, October 1963 (in the press); Akopyan, Bilesov, and Terenin, *Dokl. Akad. Nauk. S.S.S.R.*, 1961, **140**, 1037.

and Graham.¹⁹ The gases were dried (P_2O_5), nitrogen dioxide being collected in a trap cooled by solid CO_2 .

Hydrogen sulphide. The gas from iron sulphide and hydrochloric acid was passed through a saturated solution of barium hydroxide and dried (P_2O_5).

Ammonia. Cylinder ammonia gas was dried (BaO).

Methylamine. A stream of nitrogen was passed through an aqueous solution of methylamine (25% w/v). The gases were dried (BaO) and methylamine collected in a trap cooled in solid CO_2 .

Dimethyl- and trimethyl-amines. These were evolved by the action of sodium hydroxide on their hydrochlorides. These gases were dried and collected as for methylamine.

Ethyl- and isopropyl-amines. Anhydrous commercial samples were used (B.D.H.). A portion of the material was evaporated before a sample was removed for examination.

n-Butyl-, triethyl-, diethyl-, and cyclohexyl-amines and pyrrolidine. These were dried by boiling under reflux over barium oxide followed by fractional distillation, samples being taken from the middle fraction. A portion was evaporated before admission of a sample to the spectrometer.

Pyridine. This was purified by fractional distillation over potassium hydroxide and a sample was taken from the middle fraction.

Cyclohexene and pinene. These were purified by fractional distillation through a 60 cm. Vigreux column. The middle fraction was boiled under reflux with sodium for several hours and redistilled.

Cyclo-octatetraene. This was purified by the method of Cope and Hochstein.²⁰ Silver nitrate (2 g.) in water (5.0 ml.) was shaken with cyclo-octatetraene (2.0 ml.) in light petroleum (b. p. 50—60°) (5.0 ml.). The mixture was warmed to 50° to dissolve the fine crystalline precipitate, and on slow cooling precipitated a mass of large homogeneous laths. These were collected and dried in air for one min., further dried *in vacuo* on the spectrometer inlet manifold, and then cyclo-octatetraene was liberated by heating to *ca.* 170°.

n-Butane. This was prepared by Grignard reaction from n-butyl bromide in tetrahydrofuran. The product was decomposed by dilute sulphuric acid, and the evolved n-butane passed through concentrated sulphuric acid, and collected in a cooled trap (solid carbon dioxide).

n-Heptane. This was shaken with concentrated sulphuric acid, washed with water, sodium carbonate, and again with water and then fractionally distilled. The middle fraction was passed through a column of activated silica gel.

Methyl alcohol. Absolute methyl alcohol was refluxed for 4 hr. over magnesium activated by iodine, and then distilled.

Benzene and diethyl ether. Anhydrous samples were further dried over sodium.

Aldimines. Ethylidene-ethylamine, butylidene-ethylamine, and isobutylidene-ethylamine were prepared by Tiollais's method.²¹ Ethylamine was condensed with the corresponding aldehyde at 0°.

N-Isopropylidene-ethylamine. This was prepared by the procedure of Norton *et al.*²² Acetone was condensed with ethylamine at room temperature in the presence of concentrated hydrochloric acid.

All the liquid products were twice fractionally distilled, only middle fractions of correct boiling range and refractive index being used.

Cyclohexane (B.D.H. spectroscopic grade), and ethyl alcohol (absolute) were used without purification.

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¹⁹ Cottrell and Graham, *J.*, 1953, 556.

²⁰ Cope and Hochstein, *J. Amer. Chem. Soc.*, 1950, **72**, 2519.

²¹ Tiollais, *Bull. Soc. Chim. France*, 1947, **2A**, 708.

²² Norton, Hanry, Davis, Mitchwell, and Ballard, *J. Org. Chem.*, 1954, **19**, 1054.