Infrared Spectra of Arylimidazoles and Arylisoimidazoles[1]

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From a study of the infrared spectra of aryl-substituted imidazoles and 2*H*- and 4*H*-isoimidazoles, characteristic absorptions are determined which permit differentiation of the three isomeric ring systems. The sharp absorptions between 1500 and 1565 cm.$^{-1}$ are found to be most useful since the characteristic band of each of the three heterocyclic rings occurs in a region of low absorption by the others. Several other regions of the spectra are also discussed. Fourteen new arylimidazoles and arylisoimidazoles have been prepared. Included among these is 2,4,4,5-tetraphenylisoimidazole, the first example of a 4*H*-isoimidazole ring system which contains only aryl substituents.

The infrared spectra of imidazole,[2] some of its derivatives,[2] benzimidazoles,[3] and similar heterocyclic systems[4] have been described, although few correlations of characteristic bands have been reported. The infrared spectra of 2*H*- and 4*H*-isoimidazoles have not appeared in the literature. The infrared spectra of a variety of arylimidazoles and several aryl-2*H*- and 4*H*-isoimidazoles have now been examined and characteristic absorptions have been determined which can be used to characterize and differentiate between the isomeric ring systems.

Results and Discussion

The arylimidazoles which have been examined are listed in Table I; the aryl 2*H*- and 4*H*-isoimidazoles are listed in Table II. The lists include mono-, di-, tri-, and tetraarylimidazoles and arylisoimidazoles, derivatives substituted with electron-donating and electron-attracting groups, the related 2,4,5-triphenyl-1-imidazoline and imidazole.[5] The 1625–1475-cm.$^{-1}$ regions of the spectra are presented in detail (Tables I and II) and are described below. Representative spectra are shown in Fig. 1. Other regions are described when they are characteristic of a specific structure. The spectra were determined on solid samples in potassium bromide pellets since many of the materials were insoluble in appropriate solvents.

The arylimidazoles absorb in the 1625–1475 region (Table I) at approximately 1602 (m), 1585 (m–w), 1563 (w), 1538 (w), 1502 (m–s), and 1484 (s) cm.$^{-1}$. The 1602- and 1585-cm.$^{-1}$ bands, in most cases, appear to be due to the ν_{16} (E_{2g}) ring stretching vibrations for phenyl groups, some of which are partially restrained from coplanarity with the imidazole ring.[6] In the unsubstituted compounds and the halogenated derivatives (I–VIII) the higher frequency band does not occur above 1610 cm.$^{-1}$. The band is usually shifted to higher values, or a new band at approximately 1615 cm.$^{-1}$ is present, however, when other electron-donating groups are present on the 2-phenyl ring (Table I). The new band may be a result of a splitting of the degenerate ν_{16} band by the substituents into two components. The bands near 1563 and 1538 cm.$^{-1}$ are normally weak and often occur as shoulders. They do not occur so regularly as the two higher frequency bands and in some compounds are accompanied by an additional band. The 1502-cm.$^{-1}$ band is frequently strong and seldom is shifted more than ±4 cm.$^{-1}$. A band occurs in imidazole at 1498 cm.$^{-1}$ but not in certain aliphatic imidazoles (*e.g.*, 4-methylimidazole[2b]). The 1502-cm.$^{-1}$ band is present in all the substituted imidazole in Table I but is not present in the 2*H*-isoimidazoles, 2,4,5-tetraphenyl-4*H*-isoimidazole, or 2,4,5-triphenylimidazoline (XXX). Thus, the band is probably a skeletal stretching vibration of the aryl-substituted imidazole ring. The phenyl ring band which corresponds to the ν_{13} (E_{1g}) vibration of benzene is present in the arylimidazoles near 1485 cm.$^{-1}$ except in a few materials with strong electron-donating substituents (*e.g.*, both the 1500- and 1485-cm.$^{-1}$ bands are shifted to higher frequency by *ca.* 15 cm.$^{-1}$ in the tris-*p*-methyl and *p*-dimethylamino derivatives, XVI and XIX).

Aryl-2*H*-isoimidazoles (Table II, XXXI–XXXV) absorb in the 1625- to 1475-cm.$^{-1}$ region at approximately 1615 (w), 1603 (w–m), 1575 (vw), 1550 (m–s), 1537 (w–vw), and 1485 cm.$^{-1}$ (m–s). The 1615-cm.$^{-1}$ band appears to be characteristic of the aryl-2*H*-isoimidazoles.[7] The use of this band to differentiate between the isomeric ring systems is limited to some extent, however, since some imidazoles with electron-donating substituents (XI–XIV, XVI, and XIX) absorb near 1615 cm.$^{-1}$. The 1603- and 1575-cm.$^{-1}$ bands are similar to those in the arylimidazoles. All the 2*H*-isoimidazoles have the 1550 ± 2-cm.$^{-1}$ band, while only two imidazoles (V and XIX) have appreciable absorption in this region. The 1537-cm.$^{-1}$ band is normally weak and is shifted only in the *p*-anisyl derivative (XXXV). The *p*-anisyl derivative is also unique with a strong band at 1511 cm.$^{-1}$. In all of the 2*H*-isoimidazoles, a strong phenyl band occurs at 1485 cm.$^{-1}$, usually accompanied by another weaker band near 1490 cm.$^{-1}$. None of the 2*H*-isomidazoles have a band at 1502 cm.$^{-1}$, the characteristic absorption in the arylimidazole compounds.

In the 1625–1475-cm.$^{-1}$ region, 2,4,4,5-tetraphenyl-4*H*-isoimidazole (XXXVI) is similar to the aryl-2*H*-isoimidazoles with bands at 1616, 1602, 1532, and 1492 cm.$^{-1}$. Compound XXXVI differs, however, with two new strong bands at 1594 and 1563 cm.$^{-1}$.

(1) Presented in part at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963, Abstracts, p. 55M.

(2) (a) W. Otting, *Chem. Ber.*, **89**, 1940, 2887 (1956); (b) D. Garfinkel and J. T. Edsall, *J. Am. Chem. Soc.*, **80**, 3807 (1958).

(3) K. J. Morgan, *J. Chem. Soc.*, 2343 (1961), and references cited.

(4) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1958, pp. 277–285.

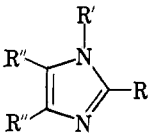
(5) The imidazole spectrum in Table I was similar to that of Otting[2a] but differed from that of Garfinkel and Edsall.[2b] The differences in the latter spectrum involved omissions of medium-to-weak bands and shifts in frequency in adjacent stronger bands. Improved resolution and exclusion of water vapor from the spectrophotometer can account for the differences.

(6) For notation and a discussion of spectra of heteroaromatic compounds, see A. R. Katritzky, *Quart. Rev.* (London), **13**, 353 (1959).

(7) The strong 1608-cm.$^{-1}$ band of the *p*-anisyl derivative XXXV prevents the determination of a band near 1615 cm.$^{-1}$.

TABLE I

INFRARED SPECTRA OF IMIIDAZOLES BETWEEN 1625 AND 1475 CM.$^{-1}$

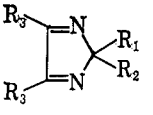


Compound	R	R′	R″	Wave numbers and relative intensity[a]							
				1615	1600	1585	1560	1540	1515	1500	1485
I	C_6H_5	H	C_6H_5		1601 m	1587 m	1565 w	1537 w		1503 s	1488 s
II	*o*-ClC_6H_4	H	C_6H_5		1602 m	1581 w	1563 wsh			1502 m	1478 s
III	*m*-ClC_6H_4	H	C_6H_5		1604 m	1584 m 1575 w	1565 vwsh	1533 vw		1503 m	1479 s
IV	*p*-ClC_6H_4	H	C_6H_5		1602 m	1583 w	1569 vwsh			1502 s	1485 s
V	2,4-$Cl_2C_6H_3$	H	C_6H_5		1600 vw	1592 m 1581 w	1572 vw	1551 m 1530 w		1501 s	1475 s
VI	2,6-$Cl_2C_6H_3$	H	C_6H_5		1604 s	1593 sh	1559 s			1502 m	1480 m
VII	*p*-ClC_6H_4	H	*p*-ClC_6H_4		1608 vw 1600 vwsh	1583 w	1557 vw			1500 s	1483 s
VIII	*o*-BrC_6H_4	H	C_6H_5		1602 m	1582 w 1575 vw	1563 w	1536 w		1503 s	1478 s
IX	*o*-Anisyl	H	C_6H_5		1600 m	1584 m	1560 vw	1527 m		1504 w	1480 s
X	*m*-Anisyl	H	C_6H_5		1604 mw 1603 m	1588 s	1565 vw	1533 w		1503 m	1485 s
XI	*p*-Anisyl	H	C_6H_5	1612 s	1603 sh		1565 vvwsh	1545 m		1506 s	1495 s
XII	*o*-HOC_6H_4	H	C_6H_5	1618 vwsh	1602 s	1583 m	1567 vw	1539 mw		1502 s	1490 s
XIII	*m*-HOC_6H_4	H	C_6H_5	1619 m	1602 m	1590 s 1582 sh		1533 w		1503 m	1482 s
XIV[b]	*p*-HOC_6H_4	H	C_6H_5	1613 m		1595 m 1575 vw		1546 w		1507 m	1491 s
XV	*p*-Tolyl	H	C_6H_5		1600 m	1586 mw 1574 w				1506 ms	1494 s
XVI	*p*-Tolyl	H	*p*-Tolyl	1618 s		1590 w			1521 s	1501 s	
XVII	α-Naphthyl	H	C_6H_5		1602 m	1587 w	1564 w		1508 s	1499 s	1475 s
XVIII	*p*-$NO_2C_6H_4$	H	C_6H_5		1600 s	1580 m		1547 vvw	1510 s	1504 ssh	1483 m
XIX	*p*-$(CH_3)_2NC_6H_4$	H	C_6H_5	1616 s	1604 sh	1585 wsh	1557 wsh	1550 ms	1509 s	1497 s	
XX	C_6H_5	H	H		1609 w	1587 vw	1570 ms 1563 m			1505 s	1475 m
XXI	H	H	C_6H_5		1602 m	1579 mw	1563 vw		1514 s	1500 ms	1485 sh
XXII	CH_3	H	C_6H_5		1602 m	1585 m		1540 s		1503 m	1475 w
XXIII[c]	C_6H_5	H	C_6H_5; H		1608 m	1583 w	1565 w	1538 w	1519 vw	1494 ms	1489 sh
XXIV	C_6H_5	C_6H_5	C_6H_5	1620 vvw	1600 s	1594 s	1560 vw		1512 w	1494 s	1479 s
XXV	C_6H_5	C_2H_5	C_6H_5		1601 m	1575 w		1550 vvw	1522 vw	1500 m	1480 m
XXVI	C_6H_5	CH_3	C_6H_5		1600 s	1577 w	1555 vvw		1519 vw	1502 s	1478 s
XXVII	*p*-Tolyl	CH_3	C_6H_5		1601 m	1583 vw 1572 vw		1530 w		1502 s	1482 s
XXVIII	C_6H_5	$C_6H_5CH_2$	C_6H_5		1601 m	1587 vw 1572 vw			1521 vw	1498 s	1480 s
XXIX	H	H	H			1576 w		1543 m		1498 m	1477 m
XXX	2,4,5-Triphenylimidazoline			1612 m	1598 m	1576 m			1510 ms		

[a] Abbreviations: w, weak; m, medium; s, strong; v, very; sh, shoulder. [b] Also absorbs at 1640 cm.$^{-1}$ (w). [c] One R″ = C_6H_5; the other R″ = H.

TABLE II

INFRARED SPECTRA OF 2*H*- AND 4*H*-ISOIMIDAZOLES BETWEEN 1625 AND 1475 CM.$^{-1}$



Compound	R_1	R_2	R_3	Wave numbers and relative intensity							
				1615	1600	1575	1563	1550	1535	1515	1485
XXXI	C_6H_5	CH_3	C_6H_5	1614 w	1602 m	1578 vvwsh 1571 vvw		1549 s	1537 sh	1527 wsh	1490 sh 1485 s
XXXII	C_6H_5	C_6H_5	C_6H_5	1614 m	1600 m	1580 vw		1550 s	1535 w	1518 vwsh	1487 s
XXXIII	—$(CH_2)_4$—		C_6H_5	1617 w	1604 w	1575 vw		1552 m	1537 w		1490 sh 1484 m
XXXIV	*p*-ClC_6H_4	CH_3	C_6H_5	1618 w	1603 w	1573 w		1552 s	1539 vw		1490 s 1484 sh
XXXV	*p*-Anisyl	CH_3	C_6H_5	1608 s	1605 wsh	1578 w		1548 m	1530 vw	1511 s	1495 vw 1485 m
XXXVI	2,4,4,5-Tetraphenyl-4*H*-isoimidazole			1616 vw	1602 ms 1594 s		1563 s		1532 m		1492 s

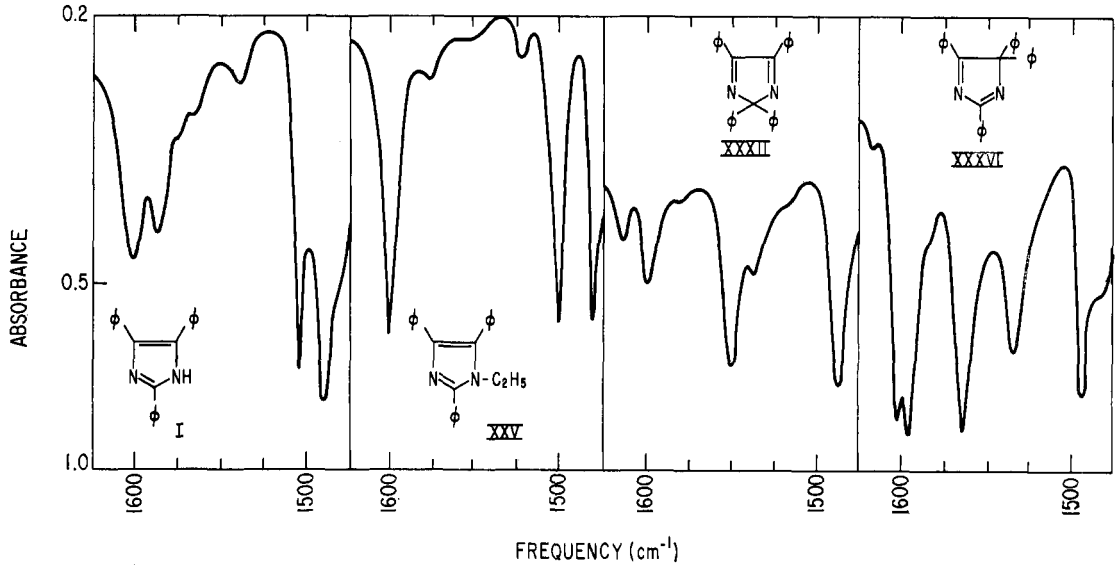


Fig. 1.—Infrared spectra of typical imidazoles and isoimidazoles between 1625 and 1475 cm.$^{-1}$.

The characteristic arylimidazole and arylisoimidazole bands between 1625 and 1475 cm.$^{-1}$ make it possible to distinguish these isomeric ring systems.[8] The 1615-(w) and 1550-cm.$^{-1}$ (m–s) bands of the 2*H*-isoimidazoles and the 1563-cm.$^{-1}$ (s) band of the 4*H*-isoimidazole occur in areas of low absorption for the aryl imidazoles. The 1502-cm.$^{-1}$ (m–s) absorption band similarly denotes the imidazole ring. The exceptions to these correlations have been noted above and normally involve compounds with electron-donating substituents. The 4*H*-isoimidazole assignment is tentative owing to the lack of additional examples.

All of the compounds containing an imidazyl N–H group displayed a characteristic absorption with a series of strong broad bands in the region 3000–2400 cm.$^{-1}$. This pattern which is observed in the solid state or relatively concentrated solution has been described previously for imidazole[9] and benzimidazole[9,10] and is attributed to coupled vibrations of strongly hydrogen-bonded aggregates.[9] The N-substituted imidazoles and the 2*H*- and 4*H*-isoimidazoles have only aromatic C–H absorptions at 3060 and 3040 cm.$^{-1}$ and in some cases appropriate aliphatic C–H bands between 3000 and 2800 cm.$^{-1}$. In addition, the N-substituted imidazoles (XXV–XXVII) have an N-alkyl C–H stretching band[11] at 2860 cm.$^{-1}$.

A number of bands other than those from phenyl or substituted phenyl groups occur consistently in the imidazoles and less consistently in the isoimidazoles. These bands are in the regions of 965, 915, 775, 720, and 705 cm.$^{-1}$ (Table III). In these compounds C–H out-of-plane deformations for unsubstituted phenyl groups usually occur at 765 and 695 cm.$^{-1}$ and for *p*-substituted phenyl groups at 835 cm.$^{-1}$.

Experimental

The infrared spectra were determined with a Beckman IR-7 spectrophotometer. Precautions were taken to avoid the presence of water vapor in the instrument. Thoroughly dried crystalline samples were analyzed in potassium bromide pellets with concentrations of approximately 6 mg./g. of potassium bromide.

Imidazole (XXIX) and **2,4,5-triphenylimidazole** (I, lophine) were obtained from Eastman Kodak Company. Other compounds which have been reported previously are listed below with pertinent analytical data for their characterization. The new compounds and their physical properties are presented in Table IV. The procedures used to prepare these compounds are described below.

The following compounds were prepared by the procedure of Davidson, Weiss, and Jelling[12] from benzil (0.05 mole), the appropriate aldehyde (0.05 mole), and 40 g. of ammonium acetate in 100 ml. of acetic acid. The procedure (A in Table IV) was modified slightly: after the reaction mixture had been heated 1 hr., water was added to the hot solution until crystals formed or clouding persisted. After cooling, the crystalline product was collected on a filter, washed, dried, and recrystallized. **2-(*o*-Chlorophenyl)-4,5-diphenylimidazole**[13] (II) was prepared in 82% yield and recrystallized from ethanol, m.p. 197.3–197.8°, lit.[14] m.p. 192°. **2-*p*-Anisyl-4,5-diphenylimidazole** (XI) was recrystallized from ethanol, m.p. 233.7–233.9°, lit.[15] m.p. 229°. **2-(*o*-Hydroxyphenyl)-4,5-diphenylimidazole** (XII) was recrystallized from aqueous ethanol, m.p. 214–215, lit.[15] m.p. 209°. **2-(*p*-Hydroxyphenyl)-4,5-diphenylimidazole**[13] (XIV) was recrystallized from aqueous ethanol, m.p. 268–268.5°, lit.[16,17] m.p. 258–259°, 256–258°. **2-(*p*-Tolyl)-4,5-diphenylimidazole** (XV) was recrystallized from ethanol, m.p. 237–237.5°, lit.[18] m.p. 233°. **2-(α-Naphthyl)-4,5-diphenylimidazole**[13] (XVII) was recrystallized from decalin, m.p. 291.5–292°, lit.[18] m.p. 283°. **2-(*p*-Nitrophenyl)-4,5-diphenylimidazole** (XVIII) was recrystallized from ethanol, m.p. 241–242°, lit.[15] m.p. 240°. **2-(*p*-Dimethylaminophenyl)-4,5-diphenylimidazole**[13] (XIX) was isolated in 71% yield and recrystallized from ethanol, m.p. 259.5–260.0°, lit.[17] m.p. 264–274°. **4,5-Diphenylimidazole** (XXI) was recrystallized from aqueous pyridine, m.p. 233–234°, lit.[12] m.p. 232°. **2-Methyl-4,5-diphenylimidazole** (XXII) was recrystallized from aqueous pyridine, m.p. 242–243.5°, lit.[12] m.p. 243°.

The following two imidazoles were prepared by the trimerization of the appropriate nitriles and reduction of the intermediate triazines with zinc and acetic acid.[15] **Tris-2,4,5-(*p*-chlorophenyl)-imidazole** (VII) was recrystallized from decalin, m.p. 275.0–275.5°, lit.[15] m.p. 268°. **Tris-2,4,5-(*p*-tolyl)imidazole**[13] (XVI)

(8) Use of these characteristic absorptions has been made in elucidating the structures of the piezochromic and photochromic dimers from oxidation of 2,4,5-triphenylimidazole (see ref. 1).

(9) L. J. Bellamy and P. E. Rogosh, *Proc. Roy. Soc.* (London), **257A**, 98 (1960).

(10) C. G. Cannon, *Spectrochim. Acta*, **10**, 341 (1958).

(11) R. D. Hill and G. D. Meakins, *J. Chem. Soc.*, 760 (1958).

(12) D. Davidson, M. Weiss, and M. Jelling, *J. Org. Chem.*, **2**, 319 (1937).

(13) Satisfactory elemental analyses were obtained.

(14) H. Bredereck, R. Gompper, and D. Hayer, *Chem. Ber.*, **92**, 338 (1959).

(15) A. H. Cook and D. G. Jones, *J. Chem. Soc.*, 278 (1941).

(16) F. R. Japp and H. H. Robinson, *Chem. Ber.*, **15**, 1269 (1882).

(17) C. V. Deliwala and S. Rajagopalan, *Proc. Indian Acad. Sci.*, **31A**, 107 (1950).

(18) B. Radziszewski, *Chem. Zentr.*, **80**, I, 1884 (1909).

TABLE III

CHARACTERISTIC IMIDAZOLE BANDS BETWEEN 1200 AND 700 CM.$^{-1}$[a]

Compound	Wave numbers and intensity					
	965	915	770	735	720	705
I	965 m	917 m	776 m	734 m	712 m	705 sh
II	968 m	910 w	775 sh	733 m	717 w	703 sh
III	967 w	917 w	779 s	727 s	722 sh	703 sh
IV	967 m	915 m	773 m	733 s	723 m	
V	969 m	913 m	776 m	737 m	723 w	705 w
VI	973 m	913 w	778 s	737 m	730 sh	712 w
VII	957 m		757 w	739 w	723 w	702 w
VIII	973 s	911 w	771 w	732 s	715 w	702 w
IX	971 w	915 w	771 m	731 w		708 w
X	967 w	917 w	777 m	732 s	725 sh	706 w
XI	966 m	912 w	773 w	738 m	724 w	708 sh
XII	976 w	912 w	776 m	742 m	725 w	708 w
XIII	971 m	914 m	779 m	730 s		705 sh
XIV	969 m	914 w	777 m	740 m	727 w	711 w
XV	967 m	913 w	774 m	731 s	725 w	707 w
XVI	968 m		767 w	737 w	728 m	708 sh
XVII	968 w	908 w	772 s	741 w	722 w	703 sh
XVIII	967 m	913 m	773 w	742 w	720 m	709 m
XIX	964 m	912 m	774 w	737 m	720 w	704 sh
XX	960 m	920 w	[a]	736 s		705 s
XXI	962 sh	912 w	779 w		722 m	702 sh
XXII	966 w	913 w	776 w	750 sh	712 w	
XXIII	963 m	913 m	775 s		715 s	
XXIV	965 w, 959 m	920 m	775 s	733 w	719 m	708 m
XXV	958 m	919 w	778 m	742 w	722 s	703 sh
XXVI	958 m	918 w	787 s	750 m	725 m	705 m
XXVII	958 m	918 w	779 s	732 s	721 w	705 m
XXVIII	962 w, 955 w	912 w	775 m	738 w	725 m, 718 m	700 sh
XXIX	938 m	924 sh, 897 w	758 m	738 w		

[a] Phenyl and substituted phenyl bands are not included and in some cases may mask out other bands.

TABLE IV

PROPERTIES OF NEW ARYLIMIDAZOLES AND ARYLISOIMIDAZOLES

Compound[a]	Procedure[b]	Yield,[c] %	Recrystn. solvent	M.p., °C.	Formula	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found	Halogen, % Calcd.	Halogen, % Found
III	A	85	Pyridine	302–304	$C_{21}H_{15}N_2Cl$	76.2	76.1	4.6	4.6	8.5	8.6	10.7	10.7
IV	A	84	Ethanol	266–268	$C_{21}H_{15}N_2Cl$	76.2	76.0	4.6	4.5	8.5	8.4	10.7	10.7
V	A	82	Ethanol	176.5–177	$C_{21}H_{14}N_2Cl_2$	69.0	69.1	3.9	3.9	7.7	7.8	19.4	19.5
VI	A	95	Ethanol	239–240	$C_{21}H_{14}N_2Cl_2$	69.0	68.6	3.9	4.0	7.7	7.9	19.4	19.3
VIII	A	99	Ethanol	207–208	$C_{21}H_{15}N_2Br$	67.2	67.3	4.0	4.2	7.5	7.7	21.3	21.1
IX	A	87	Aq. pyridine	210–210.5	$C_{22}H_{18}N_2O$	81.0	81.0	5.6	5.6	8.6	8.6		
X	A	98	Ethanol	267–268	$C_{22}H_{18}N_2O$	81.0	81.0	5.6	5.5	8.6	8.3		
XIII[d]	A	70	Ethanol	266.5–268	$C_{21}H_{16}N_2O$	80.8	80.5	5.2	5.2	9.0	9.2		
XXV[e]	B	*b*	*n*-Hexane	119.5–120	$C_{23}H_{20}N_2$	85.1	85.2	6.2	6.3	8.6	8.6		
XXVI	C	*b*	*n*-Hexane	143.5–144.5	$C_{22}H_{18}N_2$	85.1	85.3	5.8	5.8				
XXXI	D	60[f]	Aq. pyridine	114.5–115.5	$C_{22}H_{18}N_2$	85.1	85.1	5.8	5.6	9.0	9.4		
XXXIV	D	80	Methanol–benzene	154–154.5	$C_{22}H_{17}N_2Cl$	76.7	77.0	4.9	5.1	8.1	8.2		
XXXV	D	75	Benzene–hexane	128.5–129.5	$C_{23}H_{20}N_2O$	81.2	81.2	5.9	6.1	8.2	8.2		
XXXVI		*b*	Aq. pyridine	177–178	$C_{27}H_{20}N_2$	87.1	87.3	5.4	5.5	7.5	7.7		

[a] Structures are given in Tables I and II. [b] Described in the Experimental section. [c] Based on dried product after first crystallization. [d] The melting point of 182° dec. attributed to XIII by J. Tröger and H. Thomas [*J. prakt. Chem.*, **110**, 51 (1925)] indicates their material was either impure or another compound. [e] The pyrolysis product (m.p. 234°) of diethyllophine iodide described by V. Kulisch [*Monatsh.*, **17**, 300 (1896)] does not appear to be N-ethyl-2,4,5-triphenylimidazole, since the infrared and ultraviolet spectra of XXV strongly support this structure. [f] Yield after chromatography on neutral, activity I, Woelm alumina.

was recrystallized from aqueous ethanol, m.p. 240.5–241.5°, lit.[19] m.p. 235°.

The following six compounds were prepared by specific literature procedures. **2-Phenylimidazole** (XX) was recrystallized from water, m.p. 147.5–148.0°, lit.[20] m.p. 148–149°. **2,4(5)-Diphenylimidazole** (XXIII) was recrystallized from ethanol, m.p. 160–162°, lit.[21] m.p. 167–168°. **1,2,4,5-Tetraphenylimidazole** (XXIV) was recrystallized from ethanol, m.p. 220.5–221°, lit.[12] m.p. 221°. **2,4,5-Triphenylimidazoline-1** (XXX) was recrystallized from ether, m.p. 131–133°, lit.[22] m.p. 131–133°. **N-Benzyl-2,4,5-triphenylimidazole** (XXVIII) was recrystallized from ethanol, m.p. 163.5–164.5°, lit.[23] m.p. 163–164°.

N-Ethyl-2,4,5-triphenylimidazole (XXV). Procedure B (Table IV).—Ethyl bromide (10 g., 0.092 mole) was added dropwise in several minutes to a solution of 2,4,5-triphenylimidazole (10 g., 0.034 mole) and sodium (4 g., 0.17 g.-atom) in 100 ml. of ethanol at 40°. The solution was heated and a white precipitate formed. After 2 hr. at reflux, the mixture was evaporated and the solid residue was washed with water, dried, and extracted with 60 ml.

(19) A. Fürth, *Monatsh.*, **27**, 843 (1906).
(20) R. G. Fargher and F. L. Pyman, *J. Chem. Soc.*, **115**, 217 (1919).
(21) P. G. Haines and E. C. Wagner, *J. Am. Chem. Soc.*, **71**, 2793 (1949).
(22) H. H. Strain, *ibid.*, **49**, 1558 (1927).
(23) M. Weiss, *ibid.*, **74**, 5193 (1952).

of ether. Evaporation of the ether yielded a glassy foam, 1.4 g., which was dissolved in benzene and chromatographed on Woelm neutral alumina, activity I. Benzene eluted an oil which was crystallized and recrystallized from *n*-hexane, 0.6 g., m.p. 119.5–120.0°.

N-Methyl-2,4,5-triphenylimidazole (XXVI). Procedure C (Table IV).—A mixture of 2,4,5-triphenylimidazole (0.5 g., 0.0017 mole) and diazomethane (0.006 mole) in 230 ml. of ether was irradiated 1 hr. with a G.E. sunlamp after standing 5 days at 5°. After evaporation of the ether and excess diazomethane, the yellow residue was chromatographed on Woelm neutral alumina, activity I. Elution with benzene afforded a white solid (0.1 g., m.p. 135–145°) which was recrystallized from *n*-hexane, m.p. 143.5–144.5°.

N-Methyl-2-(*p*-tolyl)-4,5-diphenylimidazole (XXVII) was prepared by procedure C. The product was recrystallized from *n*-hexane, m.p. 209–215°, lit.[18] m.p. 217°.

The 2*H*-isoimidazoles were prepared by the method of Weiss[23] from benzil (0.05 mole), the appropriate ketone (0.05 mole), and 40 g. of ammonium acetate in 100 ml. of acetic acid (procedure D). **2,2,4,5-Tetraphenyl-2*H*-isoimidazole** (XXXII) was recrystallized from pyridine, m.p. 195–198°, lit.[23] m.p. 199–201°. **2,2-Spirocyclohexane-4,5-diphenyl-2*H*-isoimidazole** (XXXIII) was recrystallized from aqueous pyridine, m.p. 105.5–106°, lit.[23] m.p. 107–108°.

2,4,4,5-Tetraphenyl-4*H*-isoimidazole (XXXVI).—A dried chloroform solution of benzamidine prepared from 14.0 g. of the hydrochloride salt was refluxed for 4 hr. with 9.0 g. of diphenylbenzoylbromomethane.[24] Water was removed as formed. The reaction mixture was freed of chloroform by evaporation and the brown residue was washed three times with warm dilute ammonium hydroxide. The orange residue was taken up in benzene and filtered. The evaporated benzene solution (9.2 g.) was chromatographed on alumina, and gave rise to 6.2 g. of crude material using petroleum ether (b.p. 30–60°) and benzene as eluents. Two recrystallizations from benzene–heptane gave 2.5 g. of impure isoimidazole, m.p. 170–177°. This sample was again chromatographed on alumina and a small amount of kyaphenine, m.p. 238–238.5°, lit.[15] m.p. 232°, was removed. Recrystallization from benzene–heptane gave 1.7 g. of the isoimidazole, m.p. 177–178°. A further recrystallization from aqueous pyridine did not affect the melting point.

The structural assignment for XXXVI was based on the method of synthesis, the elemental analysis (Table IV), infrared spectrum (no N–H stretching absorption), and direct comparison with the other two possible isomers, XXIV and XXXII.

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(24) The bromo ketone [A. Werner, *Chem. Ber.*, **39**, 1286 (1906)] was prepared by refluxing diphenylbenzoylcarbinol with 32% hydrobromic acid and acetyl bromide in acetic acid for 2 hr.

Preparation of 9(11)-Unsaturated Steroids. A Novel Reagent System

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Sulfur dioxide in conjunction with various otherwise unreactive acid chlorides has been found to bring about the facile dehydration of 11β-hydroxy steroids. A rationale for this phenomenon is suggested.

Several instances are recorded in the literature[1] in which organic sulfonyl halides have been used to introduce the 9(11)-double bond into the steroid nucleus by the elimination of the elements of water from 11-hydroxylated starting materials. When the reaction involves an 11α-hydroxyl group, the intermediate sulfonic ester can be isolated and subjected to the action of a base such as pyridine or sodium acetate to complete the two-step reaction.[1a-d] Various sulfonyl halides may be used, the most common being *p*-toluenesulfonyl chloride[1a-d] and methanesulfonyl chloride.[1b] Alternatively, the reaction mixture (containing an excess of base such as pyridine) containing the sulfonic ester may be refluxed to complete the dehydration.

11β-Hydroxy steroids also respond to the action of methanesulfonyl chloride and base to furnish 9(11)-unsaturated products.[1e-g] There are two interesting points concerning this reaction. Among sulfonyl halides none except lower alkanesulfonyl halides have been made to work in the dehydration of 11β-hydroxy steroids. Furthermore, in limited cases only[2] has the isolation of the presumed intermediate 11β-mesylate been reported. The construction of a molecular model of this intermediate is at best difficult, creating some doubt that such an ester is truly a step in the mechanistic path from 11β-hydroxy steroids to 9(11)-unsaturated steroids. In addition, vigorous conditions or prolonged reaction times have been found necessary to bring about the desired reaction.[1g]

However, when mesyl chloride is distilled at atmospheric pressure prior to use, decomposition takes place in the still pot and the colorless distillate becomes a far more active agent in the dehydration reaction. Upon addition of this reagent to a cold solution of steroid, collidine, and dimethylformamide, a vigorous reaction ensues, the temperature rises, and, after a few minutes at 25–30°, the reaction is complete. Vapor phase chromatography revealed a volatile impurity in distilled mesyl chloride which was not present prior to distillation. Vacuum-distilled reagent likewise lacks the impurity and fails to bring about dehydration under the mild conditions employed. The volatile component was shown by experiment to be sulfur dioxide. Samples of mesyl chloride which failed to accomplish the desired reaction were rendered effective by the addition of small quantities of sulfur dioxide.

It may be interjected at this point that methyl chlorosulfite is also an effective agent for the elimination of the elements of water from 11β-hydroxy steroids.[1g]

(1) (a) J. Fried and E. F. Sabo, *J. Am. Chem. Soc.*, **75**, 2273 (1953); (b) **79**, 1130 (1957); (c) E. P. Oliveto, R. Rausser, L. Weber, A. L. Nussbaur, W. Gebert, C. T. Conigilio, E. B. Hershberg, S. Tolksdorf, M. Eisler, P. L. Perlman, and M. M. Pechet, *ibid.*, **80**, 4431 (1958); (d) G. Rosenkranz, O. Mancera, and F. Sondheimer, *ibid.*, **76**, 2227 (1954); (e) J. Fried, K. Florey, E. F. Sabo, J. E. Herz, A. R. Restivo, A. Borman, and F. M. Singer, *ibid.*, **77**, 4181 (1955); (f) G. E. Arth, J. Fried, D. B. R. Johnston, D. R. Hoff, L. H. Sarett, R. H. Silber, H. C. Stoerk, and C. A. Winter, *ibid.*, **80**, 3161 (1958); (g) E. M. Chamberlin, E. W. Tristram, T. Utne, and J. M. Chemerda, *J. Org. Chem.*, **25**, 295 (1960).

(2) E. J. Agnello and G. D. Laubach, U. S. Patent 2,877,157 (March 10, 1959); U. S. Patent 2,877,222 (March 10, 1959); U. S. Patent 2,877,233 (March 10, 1959). These authors report the isolation of the 11β-mesylates of $\Delta^{8(14)}$-androstene and $\Delta^{8(14)}$-19-norandrostene derivatives. Molecular models reveal that steric interference by the 18- and/or 19-methyl groups with the 11β-position is distinctly less than when the 8,14-bond is saturated.