the precipitate became sticky and decomposed. The yield of chelate diazonium fluoroborate N was 0.51 g. (55.0%). The infrared spectrum exhibited a sharp peak at 2200 cm.$^{-1}$ (diazonium ion[18]) and a peak at 1050 cm.$^{-1}$ (fluoroborate anion[19]). The diazonium salt melted at 165° with decomposition.

Anal. Calcd. for $C_{15}H_{20}O_6N_2CrBF_4$: C, 38.90; H, 4.35; N, 6.05. Found: C, 38.67; H, 4.32; N, 6.17.

Reduction of the Chelate Diazonium Fluoroborate N with Ethanol.—A solution of 50 mg. of the chelate diazonium fluoroborate N in 2 ml. of absolute ethanol was heated at reflux on the steam bath for 2 hr. After the solvent was removed under vacuum, the resulting residue was purified by chromatography on Florisil using benzene. From the benzene eluent 15 mg. of tris(2,4-pentanediono)chromium(III) (K), m.p. 201–204° (40% yield), was obtained. After recrystallization from benzene–petroleum ether, the sample melted at 210–211°. The infrared spectrum was identical with that of an authentic sample.

Pyrolysis of the Chelate Diazonium Fluoroborate N.—A mixture of 1.0 g. of the chelate diazonium fluoroborate N and 4.0 g. of powdered sodium fluoride was heated at 180–200° (oil bath temperature) for 8 hr. under vacuum (0.5 mm.) in a sublimation apparatus. The sublimate weighed 240 mg. This solid was separated by chromatography on Florisil (deactivated with 10% water) using benzene. From the second benzene eluent was obtained 50 mg. of bis(2,4-pentanediono)(3-fluoro-2,4-pentanediono)chromium(III) (O), m.p. 208–210° (6.3% yield). After recrystallization from petroleum-ether, the melting point was 212.5–213.5°. The infrared spectrum exhibited selected maxima at 1490, 1320, and 1152 cm.$^{-1}$.

Anal. Calcd. for $C_{15}H_{20}O_6FCr$: C, 49.04; H, 5.49; F, 5.17. Found: C, 48.76; H, 5.31; F, 4.72.

From the third benzene eluent 120 mg. of tris(2,4-pentanediono)chromium(III) (K), m.p. 209–211° (15.9% yield), was obtained. The infrared spectrum of this substance was identical with that of tris(2,4-pentanediono)chromium(III) (K).

Decomposition of the Chelate Diazonium Fluoroborate N in Water.—The chelate diazonium fluoroborate N (200 mg.) was dissolved in 2 ml. of water. This solution was warmed at 35–40° for 2 hr. and then extracted with a large amount of ether. The ether layer was separated and the solvent was removed under vacuum (at room temperature). The resulting residue weighed 130 mg., m.p. 121–123°. After recrystallization from ethanol-benzene, purple cubic crystals were obtained, m.p. 121–123.

Anal. Calcd. for $C_{15}H_{21}O_7Cr \cdot 12H_2O$: C, 30.97; H, 7.80. Found: C, 30.71; H, 7.60.

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[18] (a) M. Aroney, R. J. W. LeFevre, and R. L. Werner, *J. Chem. Soc.*, 276 (1955); (b) K. B. Whetsel, G. F. Hawkins, and F. E. Johnson, *J. Am. Chem. Soc.*, **78**, 3360 (1956).

[19] G. A. Olah, S. J. Kuhn, and W. S. Tolgyesi, *ibid.*, **84**, 2733 (1962).

Direct Synthesis of Ternary Iminium Salts by Combination of Aldehydes or Ketones with Secondary Amine Salts[1,2]

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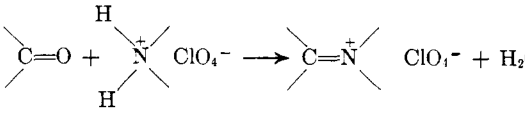
A general reaction for the preparation of ternary iminium perchlorates, $>C{=}\overset{+}{N}<ClO_4^-$, is found in the simple combination of an aldehyde or a ketone with a secondary amine perchlorate (Table I). The yields are excellent in the absence of serious steric interference. In the n.m.r. spectra of representative iminium salts, long-range coupling has been observed through three single bonds and the iminium bond and through four single bonds and the iminium bond. Mesityl oxide is converted to N-isopropylidenepyrrolidinium perchlorate (VI) by reaction with pyrrolidine perchlorate, thereby providing an efficient dealdolization process.

The importance of the $>C{=}\overset{+}{N}<\ X^-$ function in organic chemistry has been well documented by Hellmann and Opitz.[3] Immonium salts[4] or ternary iminium salts[5] (we prefer the latter name) occupy a key position in many organic reactions and are subject to rapid attack by a wide variety of nucleophilic reagents.[3,6] The salts are generally made by cleavage of a covalent C–Y bond in a $>N{-}\overset{|}{\underset{|}{C}}{-}Y$ system,[4,7] by alkylation of aldimines or ketimines,[4] and by protonation of enamines.[4,8] It is also possible to obtain ternary iminium complex salts by direct combination of an aldehyde or ketone with a secondary amine complex salt, *e.g.*; hexahalostannates,[5,9–11] halobismuthates,[5,9–10] haloantimonates,[5,9–11] hexahaloplatinates,[9,10] or iodide-silver iodide complexes.[12]

We have now found an adaptation of this procedure, which is simple and generally useful, employing the perchlorate salts of the secondary amines. Our past experience directed us to the use of these salts since the products could be expected to be easily crystallizable and nonhygroscopic and since the monovalent perchlorate anion, being a poor nucleophile, would not interfere with reaction products sought beyond the ternary iminium stage.[8b] The general reaction which can be effected is that of a ketone or aldehyde with a secondary amine perchlorate to give a ternary iminium perchlorate.



$$>C{=}O + >\overset{+}{N}H_2\ ClO_4^- \longrightarrow >C{=}\overset{+}{N}<\ ClO_4^- + H_2O \qquad (1)$$

As an example of the ease with which conversion occurs, the mixing of pyrrolidine perchlorate with a slight excess of acetone liberates heat and produces crystalline N-isopropylidenepyrrolidinium perchlorate

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[1] Supported by a research grant (USPHS-GM-05829-05) from the National Institutes of Health, U. S. Public Health Service.

[2] Presented at the 144th National Meeting of the American Chemical Society, Los Angeles, Calif., April, 1963.

[3] H. Hellman and G. Opitz, "α-Aminoalkylierung," Verlag Chemie, GMBH, Weinheim/Bergstr., Germany, 1960, p. 1, and throughout.

[4] J. Goerdeler in "Methoden der Organischen Chemie" (Houben-Weyl), Vol. XI/2, Georg Thieme Verlag, Stuttgart, Germany, 1958, pp. 616–618; see also C. R. Hauser and D. Lednicer, *J. Org. Chem.*, **24**, 46 (1959).

[5] M. Lamchen, W. Pugh, and A. M. Stephen, *J. Chem. Soc.*, 4418 (1954).

[6] N. J. Leonard and A. S. Hay, *J. Am. Chem. Soc.*, **78**, 1984 (1956), and references therein.

[7] H. G. Reiber and T. D. Stewart, *ibid.*, **62**, 3026 (1940).

[8] The following references illustrate salt formation from enamines available from different representative sources: (a) N. J. Leonard and V. W. Gash, *ibid.*, **76**, 2781 (1954); (b) N. J. Leonard and K. Jann, *ibid.*, **84**, 4806 (1962); (c) N. J. Leonard, C. K. Steinhardt, and C. Lee, *J. Org. Chem.*, **27**, 4027 (1962).

[9] W. Pugh, *J. Chem. Soc.*, 2423 (1954).

[10] M. Lamchen, W. Pugh, and A. M. Stephen, *ibid.*, 2429 (1954).

[11] G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962); see also G. Opitz, H. Hellmann, and H. W. Schubert, *ibid.*, **623**, 117 (1959).

[12] R. Kuhn and H. Schretzmann, *Ber.*, **90**, 557 (1957).

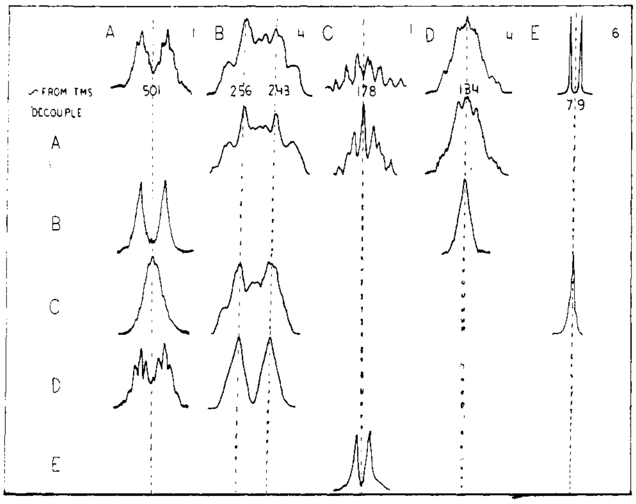
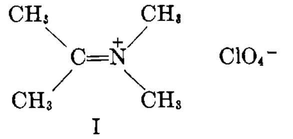


Fig. 1.—N.m.r. spin–spin decoupling with N-isobutylidenepyrrolidinium perchlorate (II).

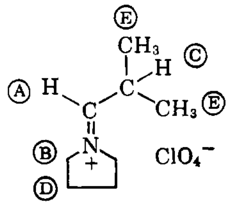
in a matter of seconds. The yield of pure product is 96% (see Experimental, procedure A). A solvent such as ethanol (1–2 vol.) also may be used. The yields are generally high for other representative ketones: ethyl methyl ketone, diethyl ketone, and cyclohexanone. Acetophenone gives the corresponding ternary iminium salt with pyrrolidine perchlorate in 70% yield, which is much greater than that obtainable by proceeding through the enamine from acetophenone and pyrrolidine followed by a separate protonation step. We expect the method to be applicable to substituted acetophenones. The perchlorate salts of other secondary amines perform in similar manner,[13] here exemplified with morpholine and dimethylamine. The product of acetone and dimethylamine perchlorate, N-isopropylidenedimethylaminium perchlorate (I), readily obtained in 92% yield, deserves special mention since it is the simplest symmetrically substituted iminium salt obtainable.


$(CH_3)_2C{=}\overset{+}{N}(CH_3)_2 \quad ClO_4^-$

I

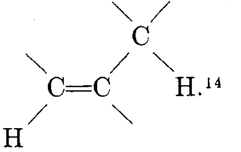
Illustrations of further scope of the reaction were obtained in the efficient condensation of cyclohexanone with morpholine perchlorate and of cyclohexanone with pyrrolidine fluoborate (see Table I). In general the fluoborate salts function less efficiently than the perchlorates but are probably handled with greater assurance of safety. Both perchlorates and fluoborates are far superior to any other secondary amine salts having representative simple anions, *e.g.*, chloride, bromide, nitrate, sulfate, which we have investigated. The condensation also can be effected in a solvent such as benzene, with azeotropic distillation of the water formed (see Experimental, procedure B). Aldehydes undergo reaction with pyrrolidine perchlorate efficiently with production of the corresponding ternary iminium salts (Table I), for which no route through an enamine—at least for the aromatic and α,β-unsaturated aldehydes—is possible. We have illustrated this facet of the reaction with benzaldehyde, isobutyraldehyde, 2-ethylbutyraldehyde, furfural, cinnamaldehyde, and pivalaldehyde. The general reaction (1) may be formulated as a nucleophilic carbonyl addition followed by the elimination of water.

All of the products have been characterized by elemental analyses, by the strong infrared absorption band indicative of $>C{=}\overset{+}{N}<$, and by the n.m.r. spectra, especially the chemical shifts for the methyl, methylene, or single protons attached to the carbon of the iminium grouping. We observed long-range coupling of these protons through the double bond with the α-methylene protons of the pyrrolidinium ring. While the n.m.r. spectra of the iminium compounds were suggestive of long-range coupling, the signals were sufficiently complex that the proton spin–spin coupling constants were not readily assignable except by double resonance experiments. The compound selected first for examination was N-isobutylidenepyrrolidinium perchlorate (II). As seen in compressed form at the top of Fig. 1, the spectrum consisted of signals, expressed in c.p.s. downfield from tetramethylsilane as 0.0, occurring at 501 (J = 9.0 c.p.s., doublet) (A), 249.5 (B), 178 (C), 134 (D), and 79 (J = 7.0 c.p.s., doublet) (E). The assignments were made as shown.



II

Where there were appreciable effects of spin–spin decoupling due to irradiation at applied frequencies corresponding to A through E, successively, the altered segments of the spectra are reproduced on the second through sixth lines in Fig. 1. The A proton was shown to be coupled to C (J_{AC} = 9.0 c.p.s.) (lines 2 and 4) and to B (J_{AB} = 2.0) (lines 2 and 3). The magnitude of J for spin–spin coupling through three single bonds and the $>C{=}\overset{+}{N}<$ double bond is in the range previously observed for long-range coupling in the system


$H{-}C{=}C{-}C{-}H$

[14] The A proton also was possibly coupled to D, since decoupling from D by irradiation at 134 c.p.s. sharpened the spectrum of A (line 5 of Fig. 1). The B protons were shown to be coupled to A and D protons (line 3). When decoupled from C, the B spectrum became sharper. Irradiation at 134 c.p.s. simplified the B spectrum to two broad singlets (line 5, see also line 3) separated by about 13 c.p.s., showing that the two α-methylene groups were not identical. The coupling of the C proton to the E protons of the methyl groups was clearly observed when irradiation at 178 c.p.s. caused the signal for the E pro-

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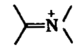
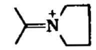
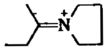
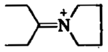
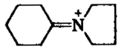
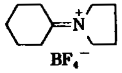
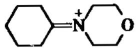
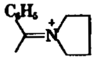
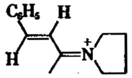
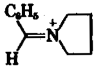
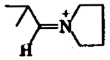
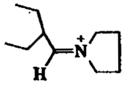
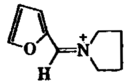
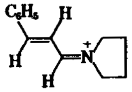
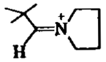
(13) Unpublished results in this laboratory by W. J. Musliner and P. C. Kelley.

(14) L. M. Jackman, "Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, Ltd., Great Britain, 1959, p. 85.

TABLE I

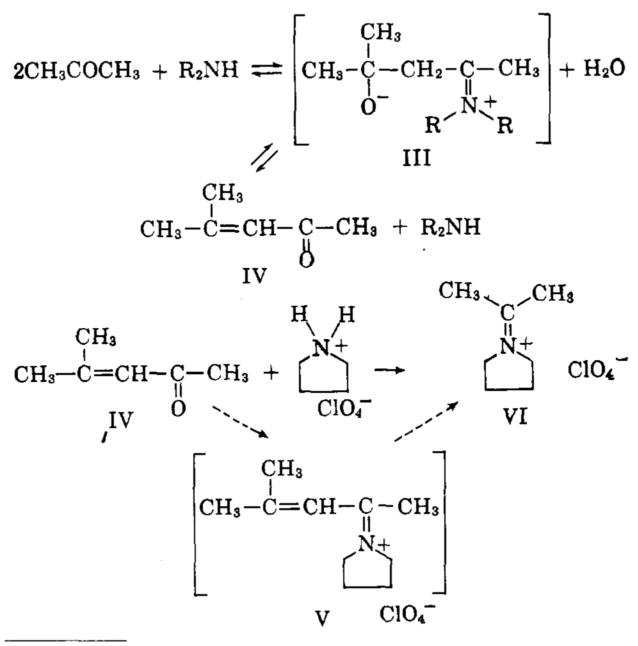
Perchlorate[a]		Procedure[b]	Yield, %	M.p., °C.	ν_{max}^{Nujol} (cm.$^{-1}$) $\overset{+}{C{=}N}$	N.m.r.		Formula	C, %		H, %		N, %	
Name	Structure					τ[d]	J[e]		Calcd.	Found	Calcd.	Found	Calcd.	Found
N-Isopropylidenedimethylaminium		A	92	298–300[c]	1687	7.53[f]	1.0	$C_5H_{12}ClNO_4$	32.35	32.42	6.52	6.54	7.55	7.55
N-Isopropylidenepyrrolidinium		A	96	232–233	1690	7.48[g]	1.4	$C_7H_{14}ClNO_4$	39.72	39.49	6.67	6.67	6.62	6.69
N-2-Butylidenepyrrolidinium		A	84	214–216	1680	7.53[h] 7.23	1.2 8.0	$C_8H_{16}ClNO_4$	42.57	42.56	7.15	7.22	6.21	6.28
N-3-Pentylidenepyrrolidinium		B	90	213–214	1665	7.22[h]	8.0	$C_9H_{18}ClNO_4$	45.10	44.93	7.57	7.58	5.85	6.11
N-Cyclohexylidenepyrrolidinium		A	90	239–240	1665	7.22[i]		$C_{10}H_{18}ClNO_4$[h]						
N-Cyclohexylidenepyrrolidinium fluoborate		B	63	220–222	1670	7.18[h]		$C_{10}H_{18}BF_4N$[h]						
N-Cyclohexylidenemorpholinium		B	94	239–241	1640	7.05[g]		$C_{10}H_{18}ClNO_5$	44.86	45.32	6.78	6.76	5.24	5.36
N-1-Methylbenzylidenepyrrolidinium		B	70	161–163	1658	7.22[g]		$C_{12}H_{16}ClNO_4$	52.65	52.40	5.90	6.04	5.12	5.13
N-1-Methylcinnamylidenepyrrolidinium		B	80	239–241	1622	7.42[f]		$C_{14}H_{18}ClNO_4$	56.10	56.38	6.05	6.11	4.67	4.67
N-Benzylidenepyrrolidinium		B	92	156–159	1658	1.01[h]	2.1	$C_{11}H_{14}ClNO_4$	50.87	50.86	5.44	5.43	5.40	5.46
N-Isobutylidenepyrrolidinium		A	92	238–240	1697	1.66[g,h]	2.0 9.0	$C_8H_{16}ClNO_4$	42.57	42.35	7.15	7.13	6.21	6.25
N-2-Ethylbutylidenepyrrolidinium		A	90	183–184	1690	1.58[h]	1.9 10.0	$C_{10}H_{20}ClNO_4$	47.33	47.12	7.95	7.83	5.52	5.61
N-Furfurylidenepyrrolidinium		A	83	99–100	1660	1.22[g] 7.04	1.8	$C_9H_{12}ClNO_5$	43.30	43.60	4.85	4.87	5.61	5.67
N-Cinnamylidenepyrrolidinium		A	87	156–157	1660	1.29[g]	1.8 10.0	$C_{13}H_{16}ClNO_4$	54.64	54.58	5.65	5.62	4.90	4.82
N-Neopentylidenepyrrolidinium		B	79[j]	307–308[c]	1682	1.73[g]	2.1	$C_9H_{18}ClNO_4$	45.10	45.21	7.57	7.66	5.85	5.68

[a] Perchlorate salt unless otherwise stated. [b] Made from the appropriate aldehyde or ketone and secondary amine salt by procedure A or B, or slight modification thereof, as indicated in the Experimental. [c] With decomposition. [d] τ values in p.p.m., for the proton on the carbon of $\overset{+}{C{=}N}$ or for the protons on the carbon alpha to the iminium carbon, with reference to tetramethylsilane as 10.0 [see G. V. D. Tiers, "Table of τ Values for a Variety of Organic Compounds," Minnesota Mining and Manufacturing Co., St. Paul. Minn., 1958; G. V. D. Tiers, *J. Phys. Chem.*, 62, 1151 (1958)]. [e] Coupling constants in c.p.s. (±0.2 c.p.s.). The first value represents the long-range coupling through the iminium double bond. The second value is for the coupling between protons on adjacent carbons on the C-side of the $\overset{+}{C{=}N}$ grouping. The major shape of the signal is that of a quintuplet. [f] Solvent: chloroacetonitrile. [g] Methylene chloride. [h] Deuteriochloroform. [i] Liquid SO₂. [j] Based on unrecovered pyrrolidine perchlorate. [k] See ref 8b.

tons to collapse from a doublet (J_{CE} = 7.0 c.p.s.) to a singlet (line 4 of Fig. 1). Similarly, irradiation at 79 c.p.s. changed the multiplet signal for the C proton to a broad doublet (bottom line), still coupled to A and perhaps B.

Another compound for which spin–spin decoupling revealed long-range splitting was N-isopropylidenedimethylaminium perchlorate (I). The n.m.r. spectrum consisted of two signals split into a quintuplet or septuplet. A decision between these possibilities was difficult because the line widths and the expected intensity ratio of 1:6:15:20:15:6:1 make the outside two peaks hard to find. Shoulders at the correct positions were observed. When the lowfield signal was followed and the highfield protons were decoupled, or *vice versa*, the remaining signal collapsed to a sharp singlet. The coupling constant, J = 1.0 c.p.s., observed was, therefore, assignable to long-range spin–spin coupling over four single bonds and one $>\!C{=}\overset{+}{N}\!<$ bond. The results obtained with N-isopropylidenedimethylaminium perchlorate (I) support the observation that in N-isobutylidenepyrrolidinium perchlorate (II) the C and B protons are involved in long-range coupling. Long-range coupling was observed in the n.m.r. spectra of all the iminium salts derived from aldehydes and methyl ketones (Table I) except N-1-methylbenzylidenepyrrolidinium perchlorate, for which the signal for the methyl group was considerably broadened but the splitting was not resolved.

In further consideration of the chemistry of iminium salts, an interesting reversal of the aldol condensation has resulted from the treatment of mesityl oxide (IV) with pyrrolidine perchlorate. An intermediate dipolar ion containing the iminium group III has been postulated to explain the specific effect of a secondary amine in the aldolization–dealdolization of acetone.[15,16] We thought it should be possible to approach this type of intermediate by condensation of mesityl oxide with pyrrolidine perchlorate, thereby forming initially the α,β-unsaturated iminium salt V. The interrelation of III and V is obvious if the former is protonated and the latter hydrated. The reaction between IV and pyrrolidine perchlorate in ethanol (1:2 mole ratio) at room temperature gave *N-isopropylidenepyrrolidinium perchlorate (VI) in 96% yield.* The dealdolization could also be effected using benzene as a refluxing solvent with azeotropic removal of water.



Experimental[17]

General Method of Preparation of Amine Salts.—To 71.1 g. (1.0 mole) of pyrrolidine in 500 ml. of ether was added perchloric acid (70% 1:1 in ethanol) until just acid to congo red. A few drops of pyrrolidine were added and the solvent was removed under vacuum. The soft solid obtained was recrystallized from 2-propanol–ether giving pyrrolidine perchlorate, colorless needles, m.p. 240–242°.

General Method of Preparation of Ternary Iminium Salts. **A.**—To 17.2 g. (0.100 mole) of pyrrolidine perchlorate in an erlenmeyer flask was added 11.6 g. (0.200 mole) of anhydrous acetone. The pyrrolidine perchlorate dissolved immediately and, on swirling, crystals separated with the evolution of heat. After a few minutes the crystals were washed with ether and recrystallized from 2-propanol, yielding 20.3 g. (96%) of N-isopropylidenepyrrolidinium perchlorate, m.p. 232–233° (Table I). Minor variations in procedure A included heating the combination of secondary amine salt and carbonyl compound when necessary and using ethanol as a solvent to dissolve the secondary amine salt before adding the carbonyl compound. The reaction could be speeded, where necessary, by addition of a few drops of the secondary amine or of a tertiary amine such as triethylamine or pyridine.

B.—To 18.8 g. (0.100 mole) of morpholine perchlorate were added 19.2 g. (0.200 mole) of cyclohexanone and 2 or 3 drops of morpholine. When no reaction was observed, 200 ml. of benzene was added and the heterogeneous mixture was heated under reflux overnight, with stirring and while removing water continuously by means of a Dean–Stark trap. The separated solid was collected by filtration, washed with ethanol and ether and dried *in vacuo*. The product, N-cyclohexylidenemorpholinium perchlorate, 25.2 g. (94%), melted at 237–239°. Recrystallization from acetonitrile–ether raised the melting point to 239–241°. The use of a Soxhlet extractor containing molecular sieves and a solvent such as chloroform for azeotroping constituted a modification of procedure B, which was successful, for example, in the combination of pyrrolidine perchlorate and diethyl ketone, giving the iminium product in 86% yield.

Dealdolization of Mesityl Oxide.—A mixture of 17.2 g. (0.10 mole) of pyrrolidine perchlorate, 4.9 g. (0.05 mole) of mesityl oxide, 5 drops of pyrrolidine, and 200 ml. of benzene was heated under reflux overnight with stirring while water was removed continuously by means of a Dean–Stark trap. The solvent was removed *in vacuo*, and the solid remaining was recrystallized from ethanol; m.p. 232–233°; yield, 19.7 g. (93%). It was identified as N-isopropylidenepyrrolidinium perchlorate (VI) by melting point, mixture melting point, infrared, and n.m.r. spectra. When excess mesityl oxide was used, the yield of the same product, based on pyrrolidine perchlorate, was unchanged.

A simpler variation, using the same amounts of pyrrolidine perchlorate and mesityl oxide as listed, with five drops of pyrrolidine, in 20 ml. of ethanol, gave N-isopropylidenepyrrolidinium perchlorate in 96% yield after 36 hr. at 25°.

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(15) I. P. Hammett, "Physical Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1940, pp. 345, 363.

(16) J Hine, "Physical Organic Chemistry," 2nd Ed., McGraw-Hill Book Co., Inc., New York, N. Y., 1962, p. 260.

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