Anal. Calcd. for $C_{19}H_{22}N_4O_8$: C, 52.53; H, 5.10; N, 12.90. Found: C, 52.30; H, 5.18; N, 12.63.

Also, **1-methyl-2-(*p*-chlorophenyl)piperidine N-oxide** was synthesized; its picrate had m.p. 186–188° after two recrystallizations from a dilute solution of picric acid in ethanol.

Anal. Calcd. for $C_{18}H_{19}ClN_4O_8$: C, 47.53; H, 4.21; N, 12.32. Found: C, 47.52; H, 4.57; N, 12.12.

Hexahydro-2-methyl-7-phenyl-1,2-oxazepine (IIIa).—1-Methyl-2-phenylpiperidine N-oxide (from 5.0 g. of the piperidine Ia) was placed in 50 ml. of dimethylacetamide, and the solution was heated at 170°. Samples were removed periodically and analyzed by gas chromatography. When no further change in the size of the IIIa peak was detected (50 min.), the reaction was stopped. Comparison of the peak area to that of a standard indicated a yield of IIIa of 59%. Two similar preparations were made, and the three products were combined for removal of solvent by distillation *in vacuo*. The residue was fractionated with a Nester–Faust spinning-band column (Model 115). The material distilling in the range 52–68° (0.3 mm.) was a mixture of Ia and IIIa, and was refractionated: (A) 3.5 g., b.p. 41–45° (0.15 mm.), 100% Ia; (B) 1.0 g., b.p. 45–52° (0.15 mm.), 30% Ia–70% IIIa; (C) 2.5 g., 53° (0.15 mm.), 3% Ia–97% IIIa; and (D) 3.0 g., 53° (0.15 mm.), 100% IIIa. The total yield of Ia was 3.9 g. (26%); of IIIa, 6.1 g. (37%); fraction D was analyzed.

Anal. Calcd. for $C_{12}H_{17}NO$: C, 75.35; H, 8.96; N, 7.32. Found: C, 75.15; H, 8.81; N, 7.28.

The picrate, recrystallized from a dilute solution of picric acid in ethanol, had m.p. 128–129°.

Anal. Calcd. for $C_{18}H_{20}N_4O_8$: C, 51.42; H, 4.80; N, 13.33. Found: C, 51.59; H, 4.91; N, 13.19.

The infrared spectrum of IIIa showed a peak of medium intensity at 923 cm.$^{-1}$, attributed to O–N stretching. The n.m.r. spectrum is described in the Discussion section; mass spectral features appear in Table II.

Hexahydro-2-methyl-7-(*p*-tolyl-1,2-oxazepine) (IIIb).—1-Methyl-2-(*p*-tolyl)piperidine N-oxide (from 8.0 g. of the piperidine Ib) was rearranged in 50 ml. of dimethylacetamide at 170°. The reaction was complete after 40 min. The ratio of IIIb to Ib was 2.2:1. This product was combined with two similar preparations (based on 8.0 g. and 5.0 g. of Ib) and distilled to remove solvent and some Ib. The fraction boiling at 90–99° (0.85 mm.) was refractionated: (A) 3.0 g., b.p. 76–90.5° (0.8 mm.), 67% Ib–33% IIIb: (B) 1.5 g., b.p. 90.5° (0.8 mm.), 2% Ib–98% IIIb; and (C) 5.5 g., b.p. 90.5° (0.8 mm.), 100% IIIb. Total yield of IIIb was 8.0 g. (35%); analysis was performed on fraction C.

Anal. Calcd. for $C_{13}H_{19}NO$: C, 76.05; H, 9.33; N, 6.82. Found: C, 76.40; H, 9.68; N, 6.67.

The picrate as formed from ethanol solution had m.p. 145.5–147°.

Anal. Calcd. for $C_{19}H_{22}N_4O_8$: C, 52.53; H, 5.10; N, 12.90. Found: C, 52.49; H, 4.88; H, 12.87.

The infrared spectrum of IIIb showed medium absorption at 924 cm.$^{-1}$. The n.m.r. spectrum contained a broad multiplet of 6H centered at 1.78, a CCH_3 singlet at 2.26, a NCH_3 singlet at 2.51, a 2H multiplet assigned to NCH_2 at 2.75, and a 1H triplet ($J = 7$ c.p.s.) at 4.74 p.p.m., assigned to the 7-proton. Mass spectral data are given in Table II.

Hexahydro-2-methyl-7-(*p*-chlorophenyl)-1,2-oxazepine.—The N-oxide from 10.0 g. of 1-methyl-2-(*p*-chlorophenyl)piperidine was rearranged as above. The ratio of IIIc to Ic was 0.43:1. The product was fractionated to provide: (A) 2.0 g., b.p. 77° (0.6 mm.), 98% Ic–2% IIIc; (B) 1.0 g., b.p. 77–86° (0.6 mm.), 50% Ic–50% IIIc; (C) 1.0 g., b.p. 86° (0.6 mm.), 10% Ic–90% IIIc; and (D) 0.5 g., b.p. 86° (0.6 mm.), 2% Ic–98% IIIc. The total yield of IIIc was 2 g. (20%). The infrared spectrum showed absorption at 925 cm.$^{-1}$. A picrate prepared from fraction D and recrystallized from a dilute solution of picric acid in ethanol had m.p. 134–135°.

Anal. Calcd. for $C_{18}H_{19}ClN_4O_8$: C, 47.53; H, 4.21; N, 12.32. Found: C, 47.32; H, 4.25; N, 12.34.

Tetrahydro-1-methyl-6-phenyl-2H-1,2-oxazine.—This compound was prepared by the reported method.[8] The boiling point was erroneously recorded[8] as 93° (0.30 mm.); the value is 78° (0.53 mm.).

Methyl(4-hexenyl)hydroxylamine.—This compound was available from the previous investigation,[8] having been obtained by pyrolysis of 1-methyl-2-ethylpyrrolidine N-oxide. Its structure was not completely established at that time, in that distinction between the presence of a 4-hexenyl or a 3-hexenyl group was not made. The n.m.r. spectrum of a benzene solution has now been prepared. The position of the methyl protons (1.59 p.p.m.) indicates the grouping $CH_3C{=}C$ rather than $CH_3CH_2C{=}C$.[6]

Acknowledgment.—Gratitude is expressed to Dr. John M. Ruth, Liggett and Myers Tobacco Company, for preparing the mass spectra and for assistance in their interpretation. F. A. S. thanks the Liggett and Myers Tobacco Company for financial assistance.

Electrolytic Reductive Coupling. IX.[1] Couplings with Representative Michael Acceptors

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Received April 20, 1965

As illustrations of the participation in electrolytic reductive coupling of a variety of Michael acceptors, data are presented on the hydrodimerization of benzalacetone, mesityl oxide, diethyl vinylphosphonate, diphenylvinylphosphine oxide, and methyl vinyl sulfone and on the mixed reductive couplings of the pairs diethyl fumarate–methyl vinyl ketone, benzalacetone–acrylonitrile, mesityl oxide–acrylonitrile, and methyl vinyl sulfone–N,N-diethylcinnamamide. The factors governing the success or failure of the method are discussed.

The scope of electrolytic reductive coupling of activated olefins was outlined in 1963.[2] Details have been published of the participation in this reaction of derivatives of α,β-unsaturated acids[3] and of butadiene,[4] of vinylpyridines,[5] and of aromatically substituted ethylenes.[6] This paper, in reporting electrolytic reductive couplings with a variety of other representative Michael acceptors, affords further confirmation of the specified synthetic utility and limitations of this method.

α,β-Unsaturated Ketones.—The electrochemical reduction of α,β-unsaturated aliphatic ketones is reported to yield hydrodimers in acid solutions and saturated monomolecular ketones in alkaline solutions.[7] The corresponding aromatic ketones give bimolecular prod-

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[1] Paper VIII: M. M. Baizer and J. D. Anderson, *J. Org. Chem.*, **30**, 1357 (1965).

[2] M. M. Baizer, *Tetrahedron Letters*, 973 (1963).

[3] M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 223 (1964); M. M. Baizer, *J. Org. Chem.*, **29**, 1670 (1964).

[4] M. M. Baizer and J. D. Anderson, *J. Electrochem. Soc.*, **111**, 226 (1964).

[5] J. D. Anderson, M. M. Baizer, and E. J. Prill, *J. Org. Chem.*, **30**, 1645 (1965).

[6] M. M. Baizer and J. D. Anderson, *ibid.*, **30**, 1348 (1965).

[7] I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. 2, Interscience Publishers, Inc., New York, N. Y., 1952, Chapter 38.

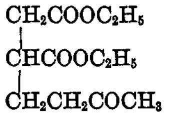
ucts in acid medium and increasing quantities of saturated ketone as the pH is raised. The proposal has been made,[8] at least for methyl vinyl ketone, that hydrodimerization occurs *via* a free radical. There appear to be no examples in the literature of mixed reductive couplings between α,β-unsaturated ketones and other activated olefins.

$$CH_3COCH{=}CH_2 + H^+ + e \longrightarrow CH_3COCH_2CH_2\cdot$$

We have studied the electrolysis, to partial conversion, of relatively concentrated solutions of α,β-unsaturated ketones (both alone and in mixtures with other activated olefins) in mildly alkaline, aqueous quaternary ammonium electrolytes. Under these conditions α,β-unsaturated ketones undergo reductive coupling, apparently *via* carbanionic intermediates according to the general scheme previously proposed for activated olefins.[2]

Benzalacetone yielded a minimum of 74% (based on current input) of the known reduced dimer 4,5-diphenyl-2,7-octanedione. Mesityl oxide formed 83% of a complex mixture of hydrodimers.[9]

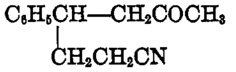
The use of α,β-unsaturated ketones in mixed reductive coupling requires comment. These ketones are excellent Michael acceptors[10] and are, therefore, suitable coupling partners for substances which are reduced at more positive cathode voltages (and thereby function as donors). A mixture of diethyl fumarate (−1.2 v.)[11] and a tenfold molar excess of methyl vinyl ketone (*ca.* −1.4 v.), for example, when electrolyzed at −1.2 to −1.3 v. gave as the major product the keto ester I.



$$\begin{array}{l} CH_2COOC_2H_5 \\ | \\ CHCOOC_2H_5 \\ | \\ CH_2CH_2COCH_3 \end{array}$$

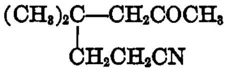
I

However, the α,β-unsaturated ketones are rather easily reduced, more easily, *e.g.*, than the corresponding α,β-unsaturated nitriles.[12] In order to compel the ketones to serve as electrochemical *donors* it is necessary to choose only those in which placement of substituents at the β-position[13] has decreased the tendency for hydrodimerization (*e.g.*, mesityl oxide) and to couple them with unencumbered exceptionally good acceptors (*e.g.*, acrylonitrile). Benzalacetone and acrylonitrile gave a poor yield of II; mesityl oxide and acrylonitrile yielded III as the major product. The coupling of 4-vinylpyridine and methyl vinyl ketone has already been reported.[5]



$$\begin{array}{l} C_6H_5CH\text{—}CH_2COCH_3 \\ | \\ CH_2CH_2CN \end{array}$$

II



$$\begin{array}{l} (CH_3)_2C\text{—}CH_2COCH_3 \\ | \\ CH_2CH_2CN \end{array}$$

III

An attempt to couple 9-benzalfluorene (donor) with mesityl oxide (acceptor) was unsuccessful, probably owing to steric effects. Electrolysis of a mixture of methyl vinyl ketone (donor) and 9-benzalfluorene (acceptor) yielded mainly the hydrodimer of the ketone and no coupled product. The hydrocarbon could not compete successfully with available ketone in capturing the postulated intermediate carbanion.

Vinylphosphonates.—Diethyl vinylphosphonate has been used as an acceptor in the Michael reaction toward a variety of donors.[10] Polarographic examination here showed that the reduction wave of the ester starts at *ca.* −2.0 v. (s.c.e.). On the basis of our previous generalization[2] it was indicated that this ester could probably be electrochemically hydrodimerized but would be a poor acceptor toward electrochemically generated carbanions. Electrolysis of a 36% solution of the ester in aqueous tetraethylammonium *p*-toluenesulfonate yielded the expected hydrodimer, tetraethyl tetramethylenediphosphonate. The current efficiency was not high because at the negative voltage required hydrogen evolution occurs unless the electrolyte is especially purified.

Vinylphosphine Oxides.—Vinylphosphine oxides are a relatively new class of compounds[14] and have only recently been employed as Michael acceptors.[15] Diphenylvinylphosphine oxide was found to reduce polarographically at $-E_{1/2}$ 2.29 v. (s.c.e.). Electrolysis of a 19% solution in a catholyte similar to the above gave a small yield of the expected hydrodimer, 1,4-tetramethylenebis(diphenylphosphine oxide). Again hydrogen evolution occurred during the electrolysis.

α,β-Unsaturated Sulfones.—Methyl vinyl sulfone prepared from methyl β-chloroethyl sulfone[16] was not completely free of starting material even after three successive treatments with triethylamine. While this impurity may not interfere when methyl vinyl sulfone is used as an acceptor in the Michael reaction[10] (since the alkaline catalyst may complete the dehydrohalogenation), it does alter the course of the reaction when the sulfone is used in electrolyses under *mildly* alkaline conditions. A sample of methyl vinyl sulfone prepared as indicated above showed two polarographic waves, one at −1.4 v. (s.c.e.) and the second at −1.8 v.[17] Electrolysis of a 33% solution of the sulfone in aqueous tetramethylammonium *p*-toluenesulfonate started at −1.4 v. and the catholyte became *acidic*. Adjustment of the pH by addition of tetraethylammonium hydroxide changed the cathode voltage to −1.6 to −1.8 where it remained for the final period of the experiment. Precipitation and gassing occurred during the reduction which, as usual, was carried to only partial conversion. The product isolated was not the expected hydrodimer IV but rather V. The formation of V may

$(CH_3SO_2CH_2CH_2\text{—})_2$ IV $\qquad$ $(CH_3SO_2CH_2\text{—})_2$ V

be rationalized by postulating that under *acid* conditions methyl vinyl sulfone had been cleaved by electrolytic

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[8] J. Wiemann, M. Monot, and J. Gordan, *Compt. rend.*, **245**, 172 (1957); J. Wiemann, *Bull. soc. chim. France*, 2545 (1964).

[9] M. Kolobielski and J. Wiemann, *Compt. rend.*, **238**, 1039 (1954).

[10] E. D. Bergmann, D. Ginsburg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

[11] Figures in parentheses refer to the voltage (*vs.* the saturated calomel electrode, s.c.e.) for the reduction of individual monomers alone. All other voltages are likewise referred to this reference electrode.

[12] Compare, *e.g.*, the reduction potentials (s.c.e.) for the following two pairs of olefins: methyl vinyl ketone (−1.43 v.) and acrylonitrile (−1.9 v.); mesityl oxide (*ca.* −1.75 v.) and β,β-dimethylacrylonitrile (*ca.* −2.03 v.).

[13] J. Kossanyi [*Compt. rend.*, **250**, 3487 (1960)] has reported that increasing the bulkiness of R in $RCOCH{=}CH_2$ also reduces tendency to hydrodimerization.

[14] R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4623 (1961).

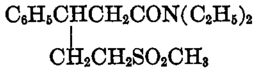
[15] M. I. Kabachnik, *et al.*, *Izv. Akad. Nauk SSSR, Otd. Khim. Nauk*, **9**, 1584 (1962); P. T. Keough and M. Grayson, *J. Org. Chem.*, **29**, 631 (1964).

[16] G. D. Buckley, J. L. Charlish, and J. D. Rose, *J. Chem. Soc.*, 1514 (1947).

[17] The first wave is probably due to reduction of chlorine.

hydrogenolysis to ethylene and methanesulfinic acid,[18] and the latter, as the acidity had moderated, had then added to the starting sulfone. The recovered methyl vinyl sulfone was free of chlorine and showed a polarographic half-wave of −1.8 v. (s.c.e.).[19]

Mixed reductive coupling of methyl vinyl sulfone and N,N-diethylcinnamamide[21] occurred at −1.7 to −1.9 v. (s.c.e.). Hydrodimer IV was obtained[22]; the evidence for the formation of the mixed product VI was not conclusive.



$$\underset{\displaystyle CH_2CH_2SO_2CH_3}{C_6H_5\overset{}{C}HCH_2CON(C_2H_5)_2}$$

VI

α,β-Unsaturated Nitro Compounds.—Polarographic examination of 2-nitro-1-butene[23] at pH 8 showed reduction waves at −0.79 and −1.47 v. (s.c.e.). Since these values are about the same as those for saturated aliphatic nitro compounds,[24] it appeared that the nitro group was being reduced before the double bond. This substance is, therefore, not a candidate for electrolytic hydrodimerization. It could be an acceptor toward an electrochemically generated carbanion if the latter were formed at more positive voltages than −0.79.

Experimental[25]

The data obtained in the hydrodimerization experiments are summarized in Table I. The results of mixed reductive coupling are described below.

Diethyl Fumarate and Methyl Vinyl Ketone.—The catholyte contained 12.0 g. (0.07 mole) of the ester, 50.0 g. (0.7 mole) of the ketone, 50 g. of tetraethylammonium *p*-toluenesulfonate, 2.0 g. of water, and 38 g. of acetonitrile. The anolyte was 16 g. of 46% methyltri-*n*-butylammonium *p*-toluenesulfonate. The electrolysis was conducted at 30°, −1.15 to −1.33 v., and an average of 0.6–0.7 amp. (total 3.56 amp.-hr.). Acetic acid (5.40 ml.) was added dropwise for pH control. Two 1-ml. portions of water were added to the catholyte in the course of the run in an attempt to improve conductivity (cell voltage 45–60). The catholyte was worked up as usual. After removal of the unreacted starting materials, the residue (23.3 g.) was vacuum distilled and the following cuts were taken: (1) 10.2 g., b.p. 100–120° (0.14 mm.), n^{25}D 1.4438; (2) 1.1 g., b.p. 124–130° (0.14 mm.), n^{25}D 1.4448; (3) 0.5 g., b.p. 135–140° (0.14 mm.), n^{25}D 1.4472; and (4) 2.0 g., b.p. 145–147° (0.18 mm.), n^{25}D 1.4534. The residue of 7.0 g. was electrolyte salt which had been coextracted. Fraction 1 was redistilled at 0.1 mm.: (1′) 1.4 g., b.p. 64–100°, n^{25}D 1.4425; (2′) 2.0 g., b.p. 100–103°, n^{25}D 1.4455; (3′) 2.9 g., b.p. 103–105°, n^{25}D 1.4430; and (4′) 1.6 g., b.p. 106–108°, n^{25}D 1.4426. Fractions 2′–4′ were found to be virtually identical by elemental analysis. Fraction 3′ was further purified by vapor phase chromatography. The material yielding the major peak (*ca.* 85%) was collected and had the correct analysis for I, diethyl α-(3-oxobutyl)maleate.

Anal. Calcd. for $C_{12}H_{20}O_5$: C, 59.02; H, 8.25; mol. wt., 244. Found: C, 59.31; H, 8.21; mol. wt., 226 ± 3%.

The proton magnetic resonance spectrum was determined at room temperature on a Varian A-60 spectrometer. Spectro Grade carbon tetrachloride was used as solvent and tetramethylsilane as internal standard. The δ values and the intensities of the signals used for the assignment of the structure are given: −1.21 (triplet for 6.0 H of $O{=}\underset{|}{C}{-}O{-}\overset{|}{\underset{|}{C}}{-}CH_3$), −1.84 [multiplet for 2.2 H of $-CH_2-C(=O)-$], −2.08 [singlet for 3.0 H of $-C(=O)-CH_3$], *ca.* −2.47 (multiplet for 5.0 H of $-CH_2-CH-CH_2-$), and −4.02 [quartet for 3.8 H of $-C(=O)-O-CH_2-C<$].

Benzalacetone and Acrylonitrile.—The catholyte contained 21.9 g. (0.15 mole) of benzalacetone, 63.6 g. (1.2 moles) of acrylonitrile, and 75 g. of tetraethylammonium *p*-toluenesulfonate. Electrolysis was conducted at 20–25°, a controlled cathode voltage of −1.43 to −1.50 v., and an amperage which was gradually reduced from 4.0 to 0.2 amp. (total 4.4 amp.-hr.). Acetic acid (1.75 moles) was used for pH control. The catholyte was worked up as usual. The residue (24.0 g.) was vacuum fractionated: (1) b.p. 117–134° (10 mm.), 1.1 g.; (2) b.p. 160 (1.4 mm.) to 164° (0.21 mm.), 1.0 g.; (3) b.p. 167–170° (0.10–0.15 mm.), 14.5 g. of benzalacetone hydrodimer; and (4) 6.3 g. of residue. Fractions 1 and 2 were combined and redistilled; the portion boiling at 138–150° (10 mm.), n^{25}D 1.5043, was collected. The analytical values were consistent with the values for slightly impure II. The structure is proposed on the basis of analogy.

Anal. Calcd. for $C_{13}H_{15}NO$: C, 77.58; H, 7.51; N, 6.96. Found: C, 77.97; H, 8.21; N, 6.71.

Mesityl Oxide and Acrylonitrile.—The catholyte contained 19.1 g. (0.195 mole) of mesityl oxide, 62.0 g. (1.17 moles) of acrylonitrile, and 78 g. of 80% aqueous tetraethylammonium *p*-toluenesulfonate. The electrolysis was conducted at 25°, a manually controlled cathode voltage of −1.65 to −1.70 v. (s.c.e.), and an amperage which was gradually reduced from 3.0 to 1.25 amp. (total 9.2 amp.-hr.). Work-up of the catholyte was as usual. The residue (40.1 g.) was fractionated *in vacuo*. After discarding foreruns (4.4 g.) boiling up to 132° (20 mm.), the major product (14.9 g.) was collected at 119–124° (5 mm.), n^{25}D 1.4459. There remained 4.0 g. of higher boiling material (adiponitrile?) and 4.2 g. of tar. The major fraction was redistilled and a center cut, b.p. 122–124° (4.7 mm.), n^{25}D 1.4460, had an analysis consistent with III.

Anal. Calcd. for $C_9H_{15}NO$: C, 70.54; H, 9.87; N, 9.14; mol. wt., 153. Found: C, 71.07; H, 10.13; N, 8.70; mol. wt. (mass spectrometer), 153.

The infrared spectrum showed $-C{\equiv}N$, $>C{=}O$, and some -OH. The latter bond may arise from some intramolecular ring closure of III.[27]

The proton magnetic resonance spectrum was determined at room temperature on a Varian A-60 spectrometer. Spectro Grade carbon tetrachloride was used as solvent and tetramethylsilane as internal standard. The δ values and the intensities of the signals used for assignment of the structure are given: −1.03 [singlet for 6.0 H of $(CH_3)_2C<$], −1.74 (multiplet for 2.3 H of CH_2-C-CN), −2.08 [singlet for 3.01 H of $-C(=O)-CH_3$], −2.32 and −2.35 [multiplet for $-CH_2$-CN and singlet for $-CH_2-C(=O)-$ with a total of 4.11 H].

Methyl Vinyl Sulfone[28] and N,N-Diethylcinnamamide.—The catholyte contained 20.3 g. (0.10 mole) of the amide, 12.7 g. (0.122 mole) of the sulfone, 50 g. of tetraethylammonium *p*-toluenesulfonate, 110 ml. of acetonitrile, and 1.0 g. of water. The anolyte was 20 g. of 60% aqueous quaternary salt solution. Electrolysis at 25–30° proceeded at an average amperage of 1.50 amp., total 6.63 amp.-hr. The cathode voltage gradually changed from −1.72 to −1.88 v. Acetic acid (5.2 ml.) was used to maintain the pH at *ca.* 8. Within the final 10 min. precipitation began occurring. The mercury was separated; the catholyte was diluted with water and filtered to remove 2.3 g. of crude II, m.p. 193°. Recrystallization from water brought the melting point to 192.5–194°. There was no depression in melting point when II was mixed with an authentic sample of 1,4-bis(methylsulfonyl)butane, m.p. 193–194° (lit.[22] 202.5–203.5°), prepared from 1,4-butanedithiol.[22] The original aqueous mother liquor was extracted with methylene chloride, etc. After removal of

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(18) E. S. Levin and A. P. Shestov [*Dokl. Akad. Nauk SSSR*, **96**, 999 (1954)] report the electrolytic cathodic cleavage of *aromatic* sulfones to sulfinic acids; see also H. V. Drushel and J. F. Miller, *Anal. Chem.*, **30**, 1271 (1958).

(19) The reported[20] value of −1.1 v. appears to be in error.

(20) C. W. Johnson, C. G. Overberger, and W. J. Seagers, *J. Am. Chem. Soc.*, **75**, 1495 (1953).

(21) Since the reduction of the amide alone occurs at *ca.* −1.7 v., three products were to be expected[3] from this reaction.

(22) C. G. Overberger and A. M. Schiller, *J. Org. Chem.*, **26**, 4230 (1961).

(23) A. T. Blomquist, *et al.*, *J. Am. Chem. Soc.*, **70**, 147 (1948).

(24) See ref. 7, p. 746.

(25) Boiling points are uncorrected. A mercury cathode was used throughout and cathode voltages are referred to the saturated calomel electrode (s.c.e.). All olefins had traces of added stabilizer. The apparatus and general procedure have been described.[26] The anolytes were always aqueous solutions of the same salt used in the catholyte. Elemental analyses of all previously reported compounds were checked and found to be satisfactory.

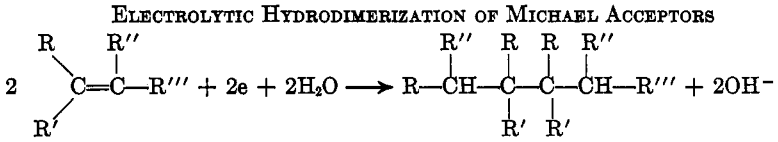
(26) M. M. Baizer, *J. Electrochem. Soc.*, **111**, 215 (1964).

(27) I. Vogel, *J. Chem. Soc.*, 598 (1927).

(28) Chlorine free.

Table I

Electrolytic Hydrodimerization of Michael Acceptors



$$2\ \underset{R'}{\overset{R}{}}\!\!>C{=}\overset{R''}{\overset{|}{C}}{-}R''' + 2e + 2H_2O \longrightarrow R{-}\overset{R''}{\overset{|}{C}}H{-}\underset{\underset{R'}{|}}{\overset{R}{\overset{|}{C}}}{-}\underset{\underset{R'}{|}}{\overset{R}{\overset{|}{C}}}{-}\overset{R''}{\overset{|}{C}}H{-}R''' + 2OH^-$$

Catholyte								-Cathode, v.	Amp.	Amp.-hr.	Temp., °C.	Product, g.
Olefin					Salt,[a] g.	Water, g.	Cosolvent, g.					
R	R′	R″	R‴	g.								
C_6H_5	H	H	$COCH_3$	81.5	82.5	20.5	None	1.26–1.31	2.3	5.1	50–60	20.8[b]
CH_3	CH_3	H	$COCH_3$	70.0	56.2	14.1	CH_3CN (22.3)	1.59–1.79	2.3	9.3	25–28	28.4[c]
H	H	H	$\overset{O}{\overset{\uparrow}{P}}(OC_2H_5)_2$	50	40.0	10.0	CH_3CN (40)	2.00–2.12	2.0	6.2	25–30	5.3[d]
H	H	H	$\overset{O}{\overset{\uparrow}{P}}(C_6H_5)_2$	30	50.0	32.5	CH_3CN (48)	2.19–2.20	1.0	3.3	30	2.0[e]
H	H	H	O_2SCH_3	50[f]	40.0	60.0	None	1.4–1.8	3.0	5.5	25	11.9[g]

[a] Tetraethylammonium *p*-toluenesulfonate. [b] Crude 4,5-diphenyl-2,7-octanedione, b.p. 188–190° (0.17–0.21 mm.). Crystallization from alcohol yielded white crystals, m.p. 163°. F. J. Dippy and R. H. Lewis [*Rec. trav. chim.*, **56**, 1000 (1937)] reported m.p. 161°. The dioxime melted at 232–234°. C. Harries and G. Eschenbach [*Ber.*, **29**, 380 (1896)] reported m.p. 235–237°. In addition, 27.5 g. of benzalacetone was recovered and a red-brown glassy residue was obtained as distillation residue. (By-products were probably due to self-condensation of the ketones under the alkaline conditions and relatively high temperatures used. At a lower temperature, as in the condensation of benzalacetone and acrylonitrile reported below, these glasses were not formed.) No benzylacetone was found (v.p.c.). [c] A mixture of hydrodimers and their transformation products[9] consisting of 12.4 g., b.p. 98–110° (20 mm.), $n^{25}D$ 1.4669; 3.2 g., b.p. 110–122° (20 mm.), $n^{25}D$ 1.4655; and 12.8 g., b.p. 123–132° (20 mm.), $n^{25}D$ 1.4660. There was virtually no distillation residue. [d] Tetraethyl tetramethylenediphosphonate, b.p. 161–166° (0.3 mm.), $n^{25}D$ 1.4445 [N. P. Bogonostseva [*Chem. Abstr.*, **51**, 6582*g* (1957)] reports b.p. 214–217° (7 mm.), $n^{25}D$ 1.4460], shown by v.p.c. retention time and infrared spectrum to be identical with an authentic sample. [e] The 1,4-butylenebis(diphenylphosphine oxide) crystallized from a concentrated methylene chloride solution, m.p. 257–260°. A. Mondon [*Ann.*, **603**, 115 (1957)] reports m.p. 257°. Starting material was recovered from the filtrate. [f] The methyl vinyl sulfone,[16] after treatment of the precursor several times with triethylamine, boiled at 55–56° (0.3 mm.), $n^{25}D$ 1.4622, and had 3.13% Cl. [g] Crude 1,2-bis(methylsulfonyl)ethane. After recrystallization from water, it melted at 190–191° and showed no depression in melting point when mixed with an authentic sample prepared from 1,2-ethanedithiol by an adaptation of Overberger and Schiller's procedures.[18] In addition 21.4 g. of chlorine-free methyl vinyl sulfone, b.p. 114–115° (18 mm.), $n^{25}D$ 1.4602, was recovered.

the solvent, an additional 1.5 g. of II was obtained by filtration. The residue was dissolved in dilute ethanol and chilled. Crude hydrodimer of the amide separated as an oil. The material remaining in the ethanol-water was re-extracted into methylene chloride and distilled. Only the 3.5 g. (VI?) boiling at 200–214° (0.15 mm.) was collected. It did not crystallize on long standing.

Anal. Calcd. for $C_{16}H_{25}NO_3S$: C, 61.70; H, 8.09; N, 4.47; S, 10.29. Found: C, 64.46; H, 8.13; N, 4.75; S, 8.20.

Acknowledgment.—Instrumental analyses were performed by Donald R. Beasecker's group. The methyl vinyl sulfone was prepared by James D. Downing.

The Configuration of Chloroacrylic Acids, Amides, Esters, and Nitriles by Nuclear Magnetic Resonance Spectroscopy

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Received April 26, 1965

The configurations of pairs of geometric isomers of derivatives of 3-chloroacrylic and 2,3-dichloroacrylic acids are established by proton magnetic resonance spectroscopy. In the two-olefinic-proton series the structural assignments are based on coupling constants and the differential shielding effect of acidic functional groups, and the spectral assignments of the AB doublets are based on a relationship of structure to absorption frequency. In the one-olefinic-proton series the structural assignments are based on the differential shielding effect of acidic functional groups.

In a recent report,[1] the specific cotton defoliating activity of *cis*-3-chloroacrylic acid and certain structural analogs was disclosed. In view of the inactivity of *trans*-3-chloroacrylic acid and certain of its structural analogs, an investigation of the effects of structure and substitution on 3-chloroacrylic acid derivatives I and II was carried out and an unequivocal basis was sought for the assignment of configuration to pairs of geometric isomers in the two-olefinic-proton series I, and the one-olefinic-proton series II. The application of n.m.r. spectroscopy to the solution of this problem was expected to resolve the two-olefinic-proton case I, since numerous publications[2] attest to the discriminatory value of n.m.r. for *cis*–*trans* olefinic protons on the basis of the spin–spin coupling constant and doublet character of the peaks.

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