of m.p. when admixed with *cis*-IV isolated from the mixture of isomers.

The *p*-bromophenacyl ester was crystallized from hexane, m.p. 90.2–90.5°. It showed no depression in m.p. with the *p*-bromophenacyl ester prepared above.

cis-3-Methoxycyclopentanecarboxylic acid (*cis*-VI). In a 300-ml. flask, equipped with stirrer, reflux condenser, and drying tube, were placed 10 g. of glass beads, 20 g. of Drierite, 50 g. of freshly precipitated anhydrous silver oxide, 150 ml. of methyl iodide, and 4.0 g. of *cis*-IV. The mixture was heated under reflux with stirring for 3 days with the addition of methyl iodide when necessary to keep the volume constant. The crude isolated material still showed a slight hydroxyl band in the infrared spectrum, so the methylation was continued for an additional 2 days with fresh silver oxide and additional methyl iodide.

The crude product, isolated by filtration, washing, and evaporation of the low boiling fraction, was treated with 100 ml. of standardized 0.8*N* sodium hydroxide and heated on the steam bath. After 45 min. the theoretical amount of base had been used, as determined by titration of an aliquot. The solution was cooled, acidified, and extracted with five 100-ml. portions of ether. The dried ether solution was distilled to afford 4.1 g. (93%) of *cis*-3-methoxycyclopentanecarboxylic acid, b.p. 136–139° (10 mm.), n_D^{26} 1.4587.

Anal. Calcd. for $C_7H_{12}O_3$: C, 58.34; H, 8.34; OCH_3, 21.52; neut. equiv., 144. Found: C, 58.16; H, 8.32; OCH_3, 21.58; neut. equiv., 145.

The *p-toluidide* was prepared by the method of Cheronis and Entriken[10] and crystallized from aqueous methanol, m.p. 81.9°.

Anal. Calcd. for $C_{14}H_{19}O_2N$: C, 72.05; H, 8.22; N, 6.00. Found: C, 72.36; H, 8.04; N, 6.58.

The *p-phenylphenacyl ester* was crystallized from aqueous ethanol, m.p. 79.5–79.7°.

Anal. Calcd. for $C_{21}H_{22}O_4$: C, 74.53; H, 6.57. Found: C, 74.36; H, 6.63.

Acknowledgments. This work was aided in part by a grant from the National Science Foundation (G-2387) and by a National Science Foundation Fellowship (to Joan S. Fessenden). We wish to thank Professor W. E. Doering for making the procedure of Vaughn available to us.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CALIFORNIA
BERKELEY 4, CALIF.

Perchlorates of Conjugate Acids of Azobenzene and Substituted Azobenzenes[1]

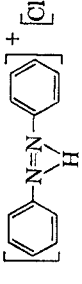
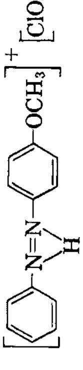
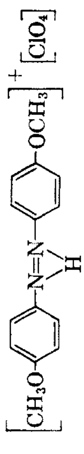
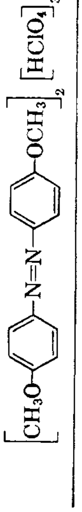
SI-JUNG YEH AND H. H. JAFFÉ

Received November 14, 1958

In an attempt to establish the structure of the conjugate acids of substituted azobenzenes, we have prepared the perchlorates of the conjugate acids of azobenzene, and of its 4-methoxy and 4,4′-dimethoxy derivatives.

TABLE I

ANALYSES AND PHYSICAL PROPERTIES OF THE PERCHLORATES

Substances	Decomposition Point, °C.[b]	Neutralization Equivalent		Analysis[a]					
				C		H		N	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
	198	284	283	50.80	50.98	4.00	3.92	9.66	9.91
	200	311	311	50.01	50.00	4.16	4.17	8.88	8.98
	205	337	343	49.22	49.20	4.52	4.42	8.06	8.19
	152	296	293	82.84	83.58	4.31	3.98	7.04	7.13

[a] Elemental analysis were performed by A. Bernhardt, Mülheim (Ruhr), Germany. [b] Uncorrected.

---

[1] This work has been supported by a Bonita Geho Memorial Grant for Cancer Research from the American Cancer Society. This support is gratefully acknowledged.

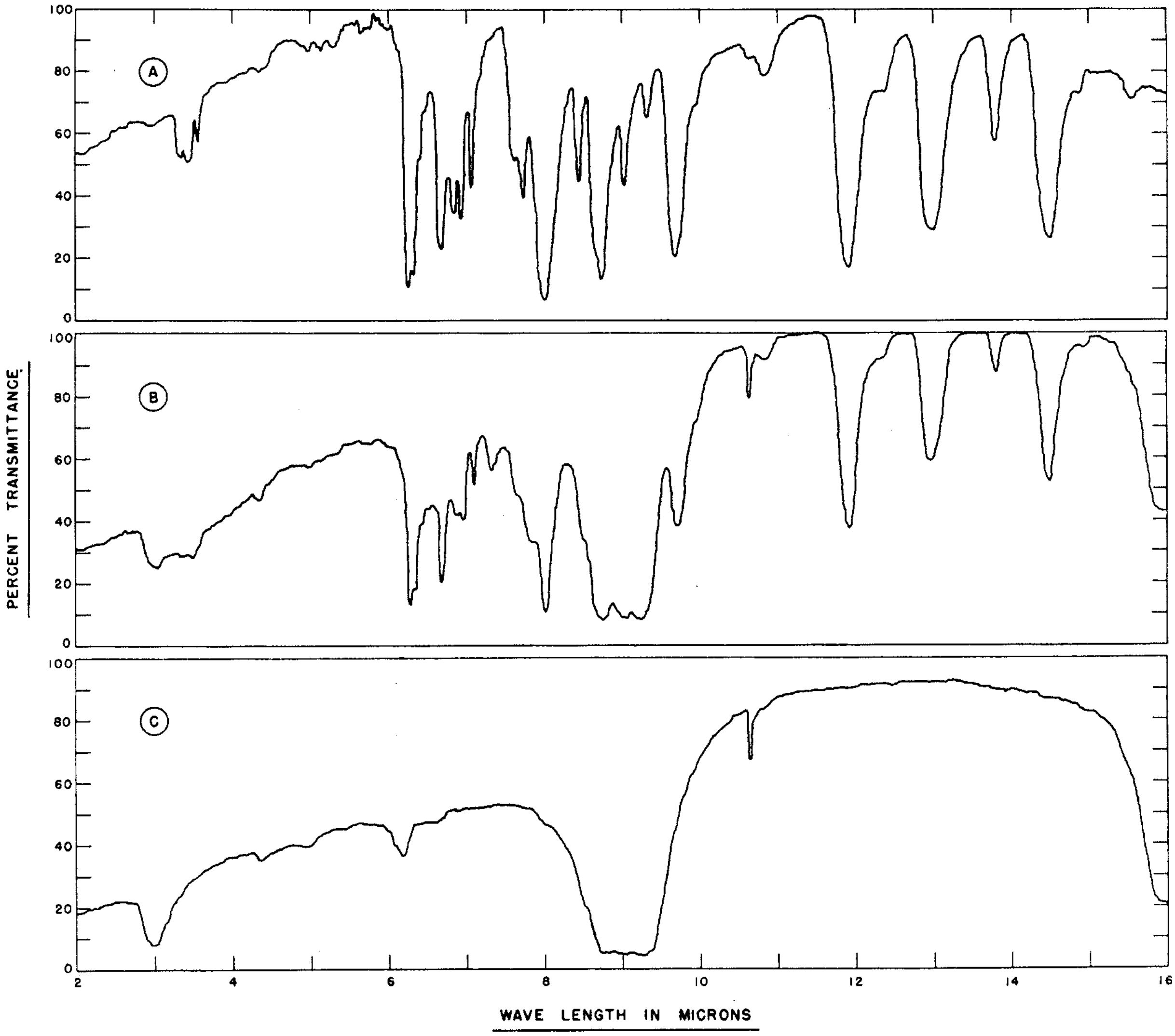
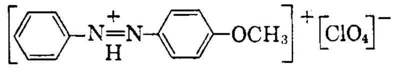


Fig. 1. Comparison of infrared spectra of (A) 4-methoxyazobenzene; (B) its salt with perchloric acid; (C) $NaClO_4$, all in KBr pellets.

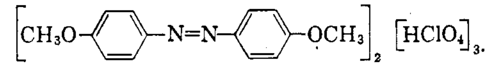
EXPERIMENTAL

Azobenzene (1 g.) was dissolved in 20 ml. of dioxane to which 50 ml. of 70% $HClO_4$ was added. Light yellow crystals precipitated and were collected on a sintered-glass filter. The perchlorate obtained was recrystallized from 70% $HClO_4$ (below 60°). The salt was highly hygroscopic, and decomposed slowly at 198°. The preliminary identification of the perchlorate was carried out by determining its neutralization equivalent, *i.e.* after hydrolysis in water the $HClO_4$ was titrated potentiometrically with standard NaOH. The results showed that exactly one equivalent of proton is associated with each mole of azobenzene. The identity of the compound was confirmed by elemental analysis, the results of which are summarized in Table I.

The perchlorate of the conjugate acid of 4-methoxyazobenzene was prepared in the same manner as that of azobenzene. After recrystallization from 70% $HClO_4$, the red crystals of the perchlorate of the conjugate acid of 4-methoxyazobenzene, decomposed slowly at 200°.



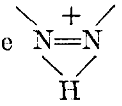
It is interesting to note the difference in the preparation of the perchlorate of the conjugate acid of 4,4'-dimethoxyazobenzene. Treatment of this compound under exactly the conditions described above, yielded very dark purple crystals which decomposed slowly at 152°. The neutralization equivalent and the elemental analysis suggested that this material was a single compound of the formula



When the perchlorate of the conjugate acid of 4,4'-dimethoxyazobenzene was prepared and recrystallized from a solution of lower acidity the monoperchlorate was obtained. 4,4'-Dimethoxyazobenzene (1 g.) was dissolved in 30 ml. of dioxane, and 10 ml. of 70% $HClO_4$ was added. The crude crystals were collected and recrystallized from 35% $HClO_4$. Golden purple crystals which decomposed at 205° were obtained. The analyses of the compounds are summarized in Table I.

Infrared spectra of the perchlorates were obtained by a Baird Model KM1 I.R. spectrophotometer. An example of the infrared spectrum is shown in Fig. 1.

DISCUSSION

We had hoped to find an NH stretching frequency, and to use this frequency to obtain information concerning the nature of the NH bond. No NH frequency was found below 3000 cm.$^{-1}$ Unfortunately, however, the spectrum of sodium perchlorate had a wide band at about 3200–3300 cm.$^{-1}$, which persisted in all the salts investigated here; this band was probably an overtone of a strong band at about 1600 cm.$^{-1}$ Consequently we were unable to observe any NH frequency in the conjugate acids of the azo compounds in the 3000–3400 cm.$^{-1}$ range, where we had anticipated that the absorption of the  $\overset{+}{N=N}$ group[2] would lie.

The infrared spectra of the compounds investigated are strikingly similar to the spectra of the free bases. Unfortunately, however, the spectra of *cis*- and *trans*-azobenzenes are so similar, that no decision can be made on the basis of these spectra concerning the stereochemistry of the conjugate acids.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF CINCINNATI
CINCINNATI 21, OHIO

---

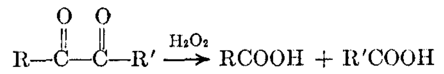
[2] H. H. Jaffé and R. W. Gardner, *J. Am. Chem. Soc.*, **80**, 319 (1958).

The Oxidation of 3,5,5-Trimethyl-1,2-cyclohexanedione by Hydrogen Peroxide

GEORGE B. PAYNE

Received November 24, 1958

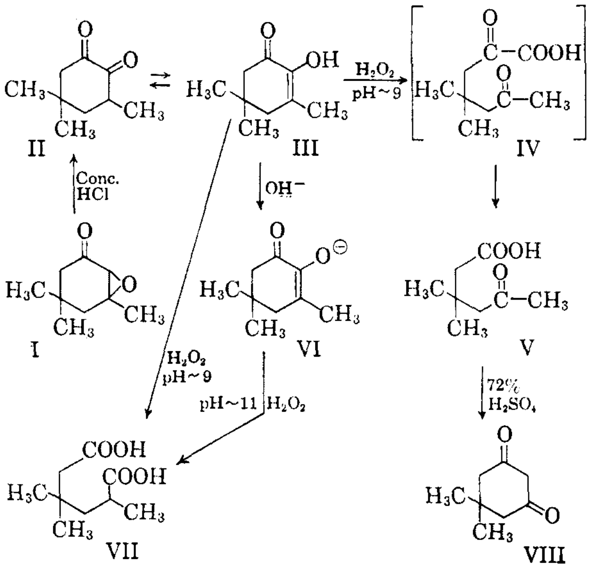
α-Diketones, on oxidation by hydrogen peroxide, are reported[1] to undergo cleavage according to the equation



$$R—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—R' \xrightarrow{H_2O_2} RCOOH + R'COOH$$

We have observed, however, that with the *cyclic* α-diketone, 3,5,5-trimethyl-1,2-cyclohexanedione (II), which, by spectroscopic evidence,[2] must exist mainly in an enolic form such as III, the product obtained with hydrogen peroxide depends on the *p*H.

Under mildly alkaline conditions (*p*H *ca.* 9), using excess hydrogen peroxide and adding alkali continuously to neutralize the acidic product, there was obtained a 26% yield of *crude* α,γ,γ-trimethyladipic acid (VII) and a 55% yield of 5-keto-3,3-dimethylhexanoic acid (V). This unexpected product was probably formed by way of the α-keto acid, IV, since carbon dioxide was evolved on acidification of the reaction mixture.[3] Its structure was indicated by physical constants and suitable analyses, and confirmed by its known[4] cyclization to dimedone (VIII).



When one molar equivalent of hydrogen peroxide was added dropwise to the enolate anion, VI (formed by charging equivalent amounts of II and alkali), a mixture resulted. Esterification of the material provided a 23% yield of diethyl α, γ, γ-trimethyl-adipate. This yield was based on unrecovered ketone.

The starting material used in this brief investigation was prepared in 65% yield from isophorone oxide (I) by treatment with cold concentrated hydrochloric acid. The oxide was prepared from isophorone in 84% yield by the action of alkaline peroxide in ethanol at 30–35°.

EXPERIMENTAL[5]

Isophorone oxide. A solution of 138 g. (1.0 mole) of isophorone (redistilled, b.p. 100–102°/20 mm.) in 1300 ml. of ethanol was charged to a 3-liter, round-bottom flask and treated with stirring with a solution of 15 g. of sodium hydroxide in 150 ml. of water. With stirring and cooling at 30–35° was added 165 g. (1.5 moles) of 30% hydrogen peroxide over a period of 20 min. After an additional hour, the mixture was diluted with 2 l. of water and extracted with three 300-ml. portions of chloroform. The combined chloroform extracts were washed with water, dried over magnesium sulfate, and distilled through a 1 × 50 cm. glass helices-packed column to give 129 g. (84% yield) of isophorone oxide, b.p. 68–69° (5 mm.), n_D^{20} 1.4539 [lit.[2a] values: b.p. 70–73° (5 mm.); n_D^{25} 1.4510].

3,5,5-Trimethyl-1,2-cyclohexanedione. To 500 ml. of concentrated hydrochloric acid stirred at 0–5° was added 100 g. (0.65 mole) of isophorone oxide. The mixture was stirred

---

[1] A. F. Holleman, *Rec. trav. chim.*, **23**, 169 (1904); J. Boeseken, *Rec. trav. chim.*, **30**, 142 (1911); E. Weitz and A. Scheffer, *Ber.*, **54B**, 2327 (1921).

[2] (a) R. L. Wasson and H. O. House, *J. Am. Chem. Soc.*, **79**, 1488 (1957); (b) H. S. French and E. T. Holden, *J. Am. Chem. Soc.*, **67**, 1239 (1945).

[3] α-Keto acids are readily cleaved by hydrogen peroxide; see ref. 1.

[4] T. Henshall, W. E. Silbermann, and J. G. Webster, *J. Am. Chem. Soc.*, **77**, 6656 (1955).

[5] All melting points are corrected.