Traynham's K_0 values for these compounds are 2,5-norbornadiene, 0.572, and 2-norbornene, 0.270.[5] The qualifications about comparing our values with his, that were discussed earlier, also apply here.) It appears, from our work, that 2,5-norbornadiene acts as a good chelater (with a fairly high K_1) and that in the formation of the complex there is little relief of strain. A picture of bonding of the chelated complexes has not been established with the definitiveness that has been done for monoölefins, and the bonding here may indeed be sufficiently different that no relief of strain in the double bond occurs.

Formation of Olefin·$(AgNO_3)_2$ Complex.—In the discussion on the development of this method, it was assumed that the formation of a 1:2 olefin–silver nitrate complex was generally negligible. This was borne out for monoölefins where the plot of H *vs.* $AgNO_3$ concentration has a decrease in slope with increasing $AgNO_3$ concentration (see Fig. 1). This same type of plot was also obtained with aromatics, alkynes and allenes which indicated that these compounds formed no appreciable amount of the 1:2 complex although they contained two or more pairs of free p-orbitals.

Although the values of K_1 for most of the diolefins studied were determined by the short one-column technique, those for four conjugated 1,3-diolefins (butadiene, isoprene, *cis-* and *trans-*1,3-pentadiene) and one non-conjugated diolefin (1,4-pentadiene) were determined by the long method involving observations on five silver nitrate columns. When H was plotted against silver nitrate concentration it was found that the slope increased with increasing silver nitrate concentration. This can be explained by assuming the presence of an appreciable reaction of these dienes with a second molecule of silver nitrate, presumably at the second double bond. This would lead to the following relationship between H and $(AgNO_3)$ for dienes

$$H = K_L + K_1K_L(AgNO_3) + K_1K_2K_L(AgNO_3)^2 - S(AgNO_3)^n$$

where K_2 is the equilibrium constant for the reaction with the second molecule of silver nitrate. Since the value of n for monoölefins has been observed to be about 2 and if we assume a similar salting-out effect for dienes, the slope of the H–$(AgNO_3)$ plot will increase if $K_1K_2K_E > S$. Since the value of S for 1-butene is 0.1 (and a similar value is expected for 1,3-butadiene since S is observed to be mainly a function of boiling point), and the value of K_1K_E for butadiene is about 10, the value of K_2 must be greater than 0.01. If the same salting-out constants are assumed for 1,3-butadiene as for 1-butene the value of K_2 for 1,3-butadiene calculates to be 0.05.

The presence of this second reaction does not interfere with the determination of K_1, since the value of $dH/d(AgNO_3)$ as $(AgNO_3)$ approaches zero for the above equation will still be equal to K_1K_L as with the first equation.

[CONTRIBUTION FROM THE EXPLOSIVES DEPARTMENT, EXPERIMENTAL STATION LABORATORY, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

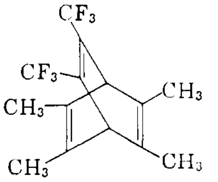
Organometallic Chemistry of the Transition Metals. I. Metal Complexes of a Bicyclo[2,2,2]octatriene Derivative

BY R. B. KING[1]

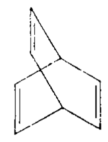
RECEIVED JULY 12, 1962

The reactions of the bicyclo[2,2,2]octatriene derivative (I), obtained from durene and hexafluorobutyne-2, with iron pentacarbonyl, cyclopentadienylcobalt dicarbonyl and molybdenum hexacarbonyl have been found to yield the complexes $C_{14}H_{14}F_6Fe(CO)_3$, $C_5H_5CoC_{14}H_{14}F_6$ and $C_{14}H_{14}F_6Mo(CO)_4$, respectively, analogous to known diene complexes of these metals. Proton and F^{19} n.m.r. data on the iron and cobalt complexes suggest the existence of isomers which involve different pairs of the three double bonds of the ligand I bonding to the metal atom.

Recently the hydrocarbon, bicyclo[2,2,2]octatriene (II)[2] ("barrelene") and certain of its substitution products such as I[3] have been reported. Since hydrocarbons with a similar arrangement of double bonds such as bicyclo[2,2,1]heptadiene (III) and 1,5-cycloöctadiene (IV) readily form diene complexes, it seemed possible that bicyclo[2,2,2]octatriene derivatives would form similar complexes utilizing two of their three double bonds in complex formation. It will be noted that there are three possible pairs of double bonds that bicyclo[2,2,2]octatriene derivatives can use in the formation of a diene complex. The existence of isomeric compounds differing only in the pair of double bonds bonded to the metal atom is therefore possible in the cases of sufficiently asymmetrical bicyclo[2,2,2]octatriene derivatives. It should be possible to distinguish such isomers



I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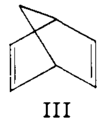
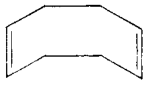

III


IV

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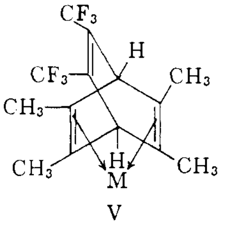
[1] Mellon Institute, 4400 Fifth Ave., Pittsburgh 13, Penna.

[2] H. E. Zimmerman and R. M. Paufler, *J. Am. Chem. Soc.*, **82**, 1514 (1960).

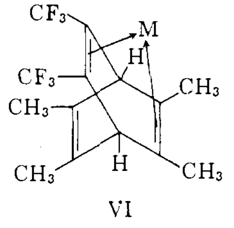
[3] C. G. Krespan, B. C. McKusick and T. L. Cairns, *ibid.*, **82**, 1515 (1960); **83**, 3428 (1961).

by physical methods such as nuclear magnetic resonance spectroscopy.

In view of these considerations it seemed of interest to investigate the reaction between a bicyclo[2,2,2]octatriene derivative and metal carbonyl derivatives known to form diene complexes. The most readily obtainable bicyclo[2,2,2]octatriene derivative is the compound I produced in one step from the reaction between durene and hexafluorobutyne-2.[3] This ligand is of special interest because two isomeric types of diene complexes are possible as represented in V and VI where M represents the metal atom to which the ligand is π-bonded. It will be noted that isomers of types V and VI should be unequivocally distinguishable by n.m.r. since in V all methyl groups are equivalent whereas in VI two different kinds of methyl groups are present in equal quantities.



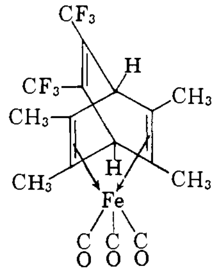
V



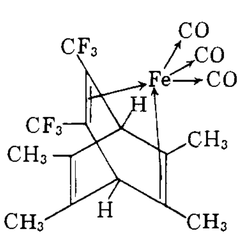
VI

Because of the great tendency for iron pentacarbonyl to react with a great variety of dienes to form complexes of the general formula (diene)-$Fe(CO)_3$,[4,5] the reaction between I and iron pentacarbonyl was first investigated and found to yield yellow volatile crystals of the composition $C_{14}H_{14}F_6Fe(CO)_3$ in about 20% yield. This compound is completely analogous to the other diene complexes derived from iron carbonyl.

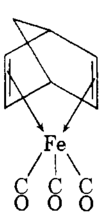
The H^1 and F^{19} n.m.r. spectra are especially revealing as to the nature of the new iron complex. In the H^1 n.m.r. spectrum sharp peaks are observed at 4.10 and 1.63 p.p.m.[6] in an intensity ratio 1:6 corresponding, respectively, to the two bridgehead protons and the twelve methyl protons in an iron complex of structure VII where the iron tricarbonyl group is bonded to the two double bonds to which methyl groups are bonded. In addition, weaker peaks are observed at 3.75, 1.75, and 1.68 p.p.m.[6] in approximate intensity ratios of 1:3:3 corresponding, respectively, to the two bridgehead protons and the two sets of six methyl protons in an iron complex of structure VIII where the iron tricarbonyl group is bonded to one double bond to which methyl groups are bonded and to one double bond to which trifluoromethyl groups are bonded. In the F^{19} spectrum resonances are observed at −540 and −335 cycles relative to internal $(CFCl_2)_2$ which on the basis of relative intensities are attributable to the CF_3 groups on the complexed double bond of VIII and the CF_3 groups on the uncomplexed double bond of VII, respectively. It is of interest that the CF_3 resonance of the free ligand I also appears at −335 cycles relative to internal $(CFCl_2)_2$ indicating that the CF_3 resonance undergoes no significant change when the double bond to which it is bonded is not involved in the π-bonding to the metal atom. On the basis of the relative intensities in these spectra the amount of VIII in the isomer mixture varied from about 10% to 25% in different samples.



VII



VIII



IX

It is of interest that the compound $C_{14}H_{14}F_6$-$Fe(CO)_3$ is only the second adequately characterized iron carbonyl complex of an unconjugated diene to be prepared. The other known complex of this type is bicyclo[2,2,1]heptadiene-iron tricarbonyl (IX).[7,8] A very unstable compound of composition $C_8H_{12}Fe(CO)_3$[5] has been reported to be formed in the reaction between 1,5-cycloöctadiene and triiron dodecacarbonyl; but in view of the tendency for iron carbonyls to catalyze the rearrangement of 1,5-cycloöctadiene to 1,3-cycloöctadiene,[9] this compound may be 1,3-cycloöctadiene-iron tricarbonyl. It appears that the tendency of iron carbonyls to cause the migration of double bonds to produce the isomeric conjugated diene is so great that iron carbonyl complexes of non-conjugated dienes can only be prepared when a diene is used in which simple migration of double bonds to produce a conjugated isomer cannot occur because of a special structural feature of the molecule. In the cases of bicyclo[2,2,1]heptadiene (III) and the bicycloöctatriene derivative I such a double bond migration would produce a hydrocarbon with a double bond on the bridgehead carbon which would be too strained for existence as a stable species.

Another carbonyl derivative which reacts with dienes to form stable derivatives is cyclopentadienylcobalt dicarbonyl.[10] The reaction between I and cyclopentadienylcobalt dicarbonyl was investigated and found to produce orange volatile crystals of composition $C_5H_5CoC_{14}H_{14}F_6$ in about 20% yield. This compound is completely analogous to other diene complexes of the type C_5H_5-Co(diene).[10]

In connection with the possible existence of the isomers X and XI of $C_5H_5CoC_{14}H_{14}F_6$, the H^1 and F^{19} n.m.r. spectra of this material were investigated. These indicated that the only isomer present in the product was XI. This is of interest since in the iron complex $C_{14}H_{14}F_6Fe(CO)_3$, the analogous isomer VIII was present only to the extent of 10–25%. The proton n.m.r. spectrum of $C_5H_5CoC_{14}H_{14}F_6$ showed resonances at approximately 4.63, 3.68,

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[4] B. F. Hallam and P. L. Pauson, *J. Chem. Soc.*, 642 (1958).

[5] R. B. King, T. A. Manuel and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **16**, 233 (1961).

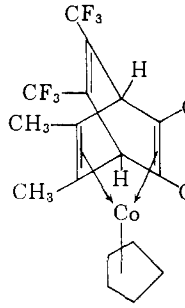
[6] H^1 chemical shifts are reported in p.p.m. downfield from tetramethylsilane.

[7] R. Burton, M. L. H. Green E. W. Abel and G. Wilkinson, *Chemistry & Industry*, 1592 (1958).

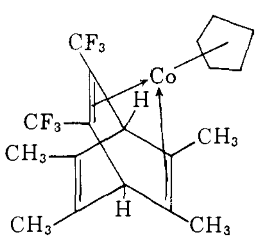
[8] R. Pettit, *J. Am. Chem. Soc.*, **81**, 1266 (1959).

[9] J. E. Arnet and R. Pettit, *ibid.*, **83**, 2954 (1961).

[10] R. B. King, P. M. Treichel and F. G. A. Stone, *ibid.*, **83**, 3593 (1961).



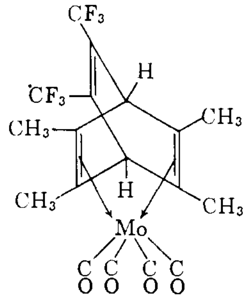
X



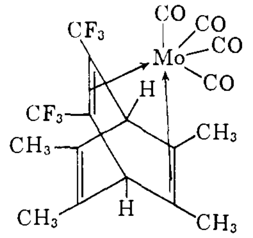
XI

1.58 and 1.55 p.p.m.[6] with approximate relative intensities of 5:2:6:6 corresponding to the five cyclopentadienyl protons, the two bridgehead protons and two sets of six methyl protons, respectively. It will be noted that the position of the resonance of the bridgehead protons at 3.68 p.p.m. in XI is much closer to the position of the corresponding protons in VIII at 3.75 p.p.m. than to the corresponding protons in VII at 4.10 p.p.m. The F^{19} spectrum of $C_5H_5CoC_{14}H_{14}F_6$ showed a single CF_3 resonance at −595 cycles relative to internal $(CFCl_2)_2$ which is closer to the resonance at −540 cycles found for VIII than to the resonance at −335 cycles found for VII.

Molybdenum hexacarbonyl also reacts with nonconjugated dienes such as 1,5-cyclooctadiene[11] and bicyclo[2,2,1]heptadiene[8] to form complexes of the type (diene)Mo$(CO)_4$. When molybdenum hexacarbonyl reacted with the bicyclo[2,2,2]-octatriene derivative I, yellow crystals of the composition $C_{14}H_{14}F_6Mo(CO)_4$ were isolated in 6% yield. The low yield of this material prevented its detailed investigation. On the basis of its infrared spectrum, which resembles that of $C_5H_5CoC_{14}H_{14}F_6$ much more closely than that of $C_{14}H_{14}F_6Fe(CO)_3$ is the C=C and C—F regions, $C_{14}H_{14}F_6Mo(CO)_4$ is believed to consist primarily of the isomer of structure XIII with little or no XII being present.



XII



XIII

Experimental

Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Infracord machine. Proton n.m.r. spectra were taken in carbon disulfide solution and recorded on the Varian Associates model A-60 machine. Chemical shifts are given in p.p.m. downfield from tetramethylsilane and were reproducible to ±0.02 p.p.m. Melting and decomposition points were determined in sealed capillaries and are uncorrected.

Bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene (I) was prepared from durene and hexafluorobutyne-2 at 200° according to the procedure of Krespan, McKusick and Cairns.[8] Cyclopentadienylcobalt dicarbonyl was prepared from sodium cyclopentadienide, cobalt(II) chloride and carbon monoxide.[10] In order to avoid the use of an autoclave in this preparation the carbonylation was carried out in the dimethyl ether of triethylene glycol (Ansul Ether 161) at atmospheric pressure at 190–210°, the cyclopentadienylcobalt dicarbonyl distilling from the reaction mixture as it was formed. Yields of once-redistilled product by this method were ~12%.

Bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene-iron Tricarbonyl.—A mixture of 3.0 g. (10 mmoles) of bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene (I), m.p. 56–58° (lit.[3] m.p. 56–57°), 5.6 ml. (7.8 g., 40 mmoles) of iron pentacarbonyl and 80 ml. of ethylcyclohexane was refluxed 63 hr. with magnetic stirring under nitrogen. The black reaction mixture was allowed to cool to room temperature and then filtered, a yellow filtrate being obtained. Solvent was removed from this filtrate at ~0.5 mm. to give yellow crystals.

These yellow crystals were dissolved in 25 ml. of pentane. The resulting yellow solution was then filtered and cooled in a −78° bath. Yellow crystals separated which were filtered and purified further by two sublimations at 70–90° (0.5 mm.) to give 890 mg. (20% yield) of yellow crystalline $C_{14}H_{14}F_6Fe(CO)_3$, m.p. 89–91.5°.

In a repeat preparation the product, having a slightly different ratio of isomers VII and VIII as shown by n.m.r., melted at 91–95°. Infrared spectrum: (bands designated by * are believed to be due to the presence of isomer VIII on the basis of their relative intensities as compared with the amount of VIII indicated to be present from the n.m.r. spectra). C–H at 2920–3020 cm.$^{-1}$ (not clearly resolved); carbonyl bands at 2070(s), 2035(s), 1990(sh, s), and 1965(s) cm.$^{-1}$; other bands at 1660(m), 1440(m), 1420(m)*, 1380(w), 1350(m), 1287(s), 1258(s)*, 1218(m), 1192(s), 1140(s), 1120(s)*, 1035(m), 1020(m), 1007(m), 966(w), 909(w) and 682(w) cm.$^{-1}$; n.m.r. spectra: see Discussion section.

Anal. Calcd. for $C_{17}H_{14}F_6O_3Fe$: C, 46.8; H, 3.2; F, 26.2; Fe, 12.9; mol. wt., 436. Found (two independent preparations where duplicate analyses are given): C, 46.9, 47.4; H, 3.3, 3.6; F, 25.9; Fe, 13.4; mol. wt., 473 (isopiestic in dichloromethane).

Cyclopentadienylcobalt Bis-(trifluoromethyl)-bicyclo-[2,2,2]octatriene.—A mixture of 1.0 ml. (~1.4 g., ~8 mmoles) of cyclopentadienylcobalt dicarbonyl, 1.5 g. (5 mmoles) of bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]-octatriene (I) and 40 ml. of ethylcyclohexane was refluxed 88 hr. under nitrogen with magnetic stirring. The reaction mixture was allowed to cool to room temperature and the solvent removed at ~0.25 mm. The resulting brown residue was shaken with 40 ml. of pentane and the yellow-orange solution filtered. The filtrate was cooled for 2 hr. in a −78° bath. The resulting orange solid was filtered and purified further by sublimation at ~100° (0.1 mm.) giving 430 mg. (20% yield) of orange crystalline $C_5H_5CoC_{14}H_{14}F_6$, m.p. 160–161.5°; infrared spectrum: C–H bands at 3010(w), 2920(w) and 2870(vw) cm.$^{-1}$; no carbonyl bands; other bands at 1432(s), 1375(w), 1346(m), 1317(m), 1285(m), 1255(s), 1229(m), 1214(m), 1186(m), 1162(m), 1134(s), 1118(s), 1107(s), 1093(s), 1032(m), 1027(m), 996(m), 980(vw), 950(vw), 940(w), 902(m), 860(w), 822(s), 780(vw), 764(vw), 730(vw), and 688(w) cm.$^{-1}$; n.m.r. spectra: see Discussion section.

Anal. Calcd. for $C_{19}H_{19}F_6Co$: C, 54.3; H, 4.5; Co, 14.1. Found: C, 54.8; H, 4.6; Co, 13.4.

Bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene-molybdenum Tetracarbonyl.—A mixture of 1.5 g. (5 mmoles) of bis-(trifluoromethyl)-tetramethylbicyclo-[2,2,2]octatriene (I), 1.32 g. (5 mmoles) of molybdenum hexacarbonyl and 40 ml. of ethylcyclohexane was refluxed 64 hr. under nitrogen with magnetic stirring. The reaction mixture became black. After the reaction period was over the reaction mixture was allowed to cool to room temperature and solvent removed at 0.1 mm. leaving a sticky black residue. After washing with 15 ml. of pentane at −78° this residue was transferred to a sublimer and sublimed at 100° (0.25 mm.) for 16 hr. to give 150 mg. (6% yield) of bright yellow crystalline $C_{14}H_{14}F_6Mo(CO)_4$ which on heating decomposed at 120–121° becoming black; infrared spectrum: C–H bands at 3000–2950(vw) and 2890(vw, sh) cm.$^{-1}$; carbonyl bands at 2060(vs), 1980(vs), 1940(vs) and

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[11] T. A. Manuel and F. G. A. Stone, *Chemistry & Industry*, 1349 (1959); E. O. Fischer and W. Fröhlich, *Ber.*, **92**, 2995 (1959); M. A. Bennett and G. Wilkinson, *Chemistry & Industry*, 1516 (1959).

1930(vs) cm.$^{-1}$; other bands at 1441(s), 1382(w), 1336(m), 1320(vw), 1288(m), 1258(s), 1229(m), 1215(m), 1173(s), 1145(s), 1120(s), 1035(m), 987(m), 951(vw), 905(w), 767(w), and 736(w) cm.$^{-1}$.

Anal. Calcd. for $C_{18}H_{14}F_6O_4Mo$: C, 42.9; H, 2.8. Found: C, 42.9; H, 2.9.

Acknowledgment.—The author wishes to acknowledge the suggestions of Dr. C. G. Krespan of the Central Research Department of du Pont in connection with the preparation of the bis-(trifluoromethyl)-tetramethylbicyclo[2,2,2]octatriene.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CINCINNATI, CINCINNATI 21, OHIO]

The Structures of the Conjugate Acids of *cis*- and *trans*-Azobenzenes[1]

BY J. H. COLLINS[2] AND H. H. JAFFE

RECEIVED DECEMBER 28, 1961

The basicities of seven *cis–trans* pairs of monosubstituted azobenzenes have been measured in an acetic acid medium. σ-Values were required to obtain a good fit of the data for the *cis* isomers, while σ^+-values were needed to correlate the *trans* constants. These results are given the interpretation that the *cis* compounds are electronically and structurally related to anilines, and that the benzene rings in these molecules are not far from being perpendicular to the —N=N— plane. A careful mathematical and statistical analysis of the data which lead to the previously proposed delocalized bonding structure of the *trans* conjugate acid is also reported.

In earlier papers,[3] we have proposed that the structure of the conjugate acid of *trans*-azobenzene involves delocalized bonding of the proton to the azo group rather than a localized N–H bond. We arrived at this conclusion from an analysis of pK data, which seem to indicate that the behavior of unsymmetrically substituted derivatives of *trans*-azobenzene was not that expected of a tautomeric mixture of α- and β-protonated species. As a corrollary to our conclusion, we proposed that the conjugate acid of *trans*-azobenzene might have a *cis* configuration. Uncontrovertible evidence has since been produced that the conjugate acid of *cis*-azobenzene, formed by treatment of this compound with strong acid, has properties different from those of the *trans* conjugate acid.[4] The same conclusion was suggested by experiments performed in this Laboratory, in which we failed to obtain *cis*-azobenzene by neutralization of the conjugate acid of its *trans* isomer at Dry Ice temperature. Consequently the corollary to our conclusion must be abandoned; the arguments which led to our original conclusion will be critically re-examined in this paper by the use of careful mathematical and statistical analysis of the data.

Also in order to obtain a better understanding of the electronic and structural nature of the *cis* and *trans* configurations of azobenzene, the basicities of seven *cis–trans* pairs of substituted azobenzenes have been measured by spectrophotometric methods. Because of the instability of the *cis* isomers in strongly acidic aqueous solution, measurements were made in a non-aqueous medium consisting of perchloric acid in acetic acid.[5] The *cis* isomers were quite stable in this medium; no *cis–trans* conversion was observed during the measurements. The constants reported in this paper, determined by standard spectrophotometric methods,[6] represent the equilibrium

$$B + HClO_4 \overset{K}{\rightleftarrows} BH^+ClO_4^- \rightleftarrows BH^+ + ClO_4^-$$

$$K = \frac{\Sigma[BH^+]}{[B][HClO_4]}$$

and will be reported as association constants.

Since the basicities of the *trans* isomers in aqueous acid solution have already been determined in this Laboratory,[3] measurement of $K_{\text{assoc.}}$ in acetic acid permits estimation of the pK_a's of the *cis* compounds, on the assumption that the relation between the two solvent systems is the same for the two configurations.

Experimental

trans-**Monosubstituted azobenzenes** were prepared by the condensation of nitrosobenzene with the appropriately substituted anilines.[3] Purification was achieved by chromatography on alumina followed by recrystallization, usually from aqueous alcohol.

cis-**Monosubstituted Azobenzenes.**—A solution of a *trans* isomer was irradiated with ultraviolet light for a period of about 1 hour, after which the equilibrium mixture of *cis* and *trans* isomers formed was chromatographed on a column of alumina to afford separation. The *trans* isomer was washed from the column while the *cis* isomer remained absorbed. The *cis* compound was then eluted from the column with anhydrous ether, isolated from the solution by evaporation to dryness at room temperature, and then recrystallized from petroleum ether (60–90° fraction). Care was taken to allow the *cis* compounds to be in solution only for a minimum length of time.

The solvents used for the chromatographic separations varied from petroleum ether to benzene through a series of mixtures of the two. In preparing *p*-acetyl, *p*-cyano- and *m*-nitro-*cis*-azobenzene a third product was separated in small yields from the irradiated mixtures; this compound was undoubtably some decomposition product, and could only be separated from the *cis* isomer by the use of a proper chromatographic solvent. A 1:1 mixture of petroleum ether and benzene was found to be successful for the *p*-acetyl and *p*-cyano compounds and petroleum ether alone was used for the *m*-nitro compound. No attempt was made to identify the decomposition products.

These isomers were identified by their ultraviolet spectra and by analysis. Data on the *cis* and *trans* compound which were prepared are listed in Table I.

Standard Acid Solution.[5]—Standard solutions of perchloric acid were prepared by adding a calculated amount of 70% perchloric acid to 300 ml. of spectroscopic grade glacial

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[1] Presented in part before the Organic Division of the American Chemical Society in Chicago, Ill., September, 1961.

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