intermediates in irradiated water, and no attempt will be made to cover this complex subject here. Clear evidence that one of these species is a negatively charged one has been obtained recently by Czapski and Schwarz,[9] and by Collinson, Dainton, Smith and Tazuké.[10] We use the terminology of Platzman and call this species the hydrated electron, and designate it by e_{aq}^-. While our work is still only in a preliminary state, it is nevertheless possible to draw some conclusions of interest to radiation chemists.

Since the spectra we have obtained are identical in neutral water and in alkaline solutions up to pH 12, it is clear from our results that the hydrated electron exists for microseconds in the pH range from 7 to 12, even at dose rates of 12 kilorads per pulse. And since the spectrum is faint at best in acid solutions, we deduce that the major fraction of hydrated electrons reacts with hydrogen ions in less than a microsecond according to

$$e_{aq}^- + H_3O_{aq}^+ \longrightarrow H + H_2O$$

Other reactions readily occurring in neutral and alkaline solutions are of the hydrated electron with oxygen, carbon dioxide, nitrous oxide, hydrogen peroxide and the formate ion.

The results presented above show that the revealing method of spectroscopy can be used for the investigation of the physical and chemical properties of the hydrated electron. The solvated electron may also be produced by ionizing radiation in ammonia and the alkyl amines, and so this method may be used for studies of its properties in these media too.

We are grateful to Dr. G. E. Adams for much help in evaluating the spectra, to him and to Dr. L. H. Gray and Dr. R. L. Platzman for several stimulating discussions of the results, and to Miss P. Walsh and Mr. J. Dyer for technical help in the experiments. The work was done while E. J. H. was on a research assignment at the Research Unit in Radiobiology of the British Empire Cancer Campaign.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ROCHESTER, ROCHESTER 20, N. Y.]

The Migration Aptitude of Benzyl *vs.* Methyl in Carbonium Ion Reactions of the 2,2-Dimethyl-3-phenyl-1-propyl System[1]

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The rearrangement of 2,2-dimethyl-3-phenyl-1-propyl *p*-toluenesulfonate (Ia) by refluxing in formic acid and in acetic acid and of 2,2-dimethyl-3-phenyl-1-propylamine (Ib) by treatment with sodium nitrite in acetic acid yielded mixtures of olefins and esters. The mixtures, after treatment with lithium aluminum hydride, were analyzed by gas chromatography and infrared and ultraviolet spectroscopy. Migration aptitudes of methyl/benzyl of 3.5, 3.2 and 2.1 were obtained for acetolysis, formolysis and deamination, respectively. Benzyl has an electron-withdrawing inductive effect relative to methyl, and this is probably the main reason for its lower tendency to migrate.

We undertook a careful study of the migration aptitude of benzyl because the behavior of this group should shed special light on the mechanism of migration of alkyl groups. In migrations to oxygen, benzyl migrates considerably better than other primary alkyl groups, which suggests that it possesses some carbonium-ion character in the transition state.[2] Whether a similar situation obtains in carbonium-ion rearrangements was not clear. House[3] found that methyl migrates better than benzyl in the diazomethane–ketone reaction and in amino alcohol deamination. A number of other reactions are reported to give the opposite result,[4] though the methods available to these early workers were insufficiently quantitative to permit reliable conclusions.

For these reasons, we chose to re-examine the system with 2,2-dimethyl-3-phenyl-1-propyl.[4b] This neopentyl-like carbon skeleton would be expected to undergo complete rearrangement to stable products in a carbonium-ion reaction with minimum opportunity for steric complications at the migration terminus. The reactions studied were formolysis and acetolysis of the tosylate, and nitrous acid deamination of the amine. The product mixtures were analyzed by means of gas chromatography and ultraviolet and infrared spectroscopy.

The starting materials were synthesized by the following scheme. Methyl isobutyrate and benzyl chloride were condensed using sodium hydride as the base.[5] The resulting ester, methyl 2,2-dimethyl-3-phenylpropionate, was reduced with lithium aluminum hydride and the alcohol Ic was treated with *p*-toluenesulfonyl chloride in pyridine to produce Ia. Hydrolysis of methyl 2,2-dimethyl-3-phenylpropionate, followed by treatment with thionyl chloride and ammonium hydroxide in subsequent steps, gave 2,2-dimethyl-3-phenylpropionamide. Reduction of the amide with lithium aluminum hydride produced 2,2-dimethyl-3-phenyl-1-propylamine (Ib).

Since product analysis was to be done by gas chromatography, reference samples of the various

(1) This work was supported in part by the U. S. Army Research Office (Durham). P. Warrick received stipends from the Hooker Fund and the Charles Pfizer and Co., Inc., grant.

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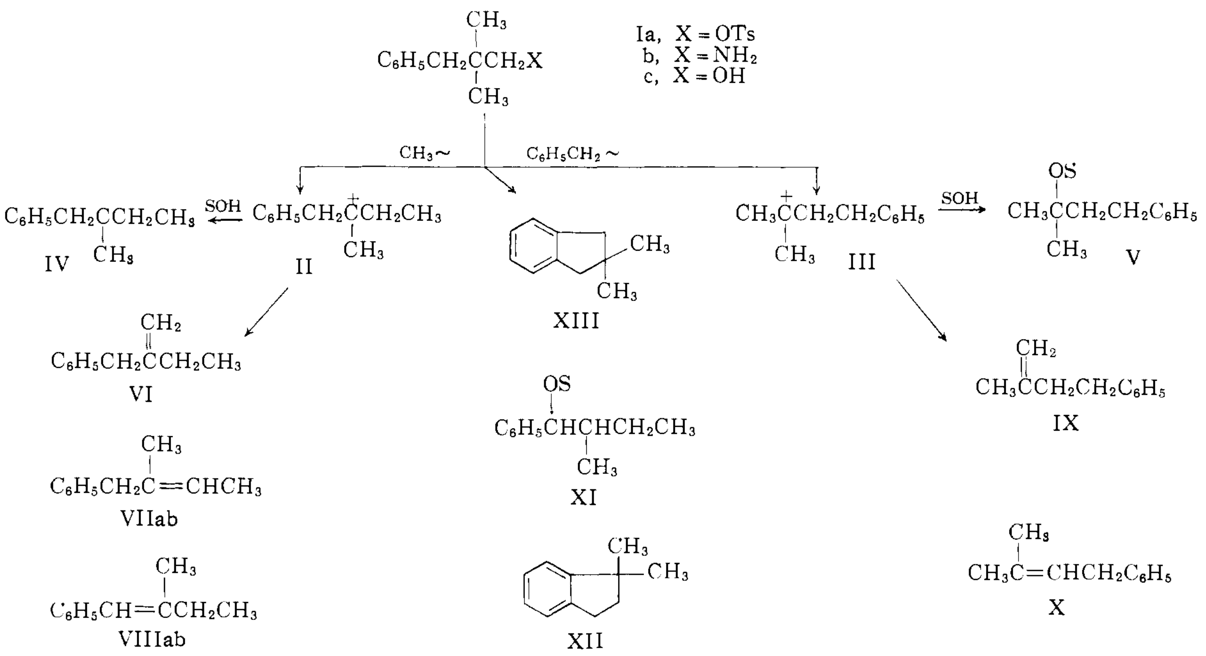

Fig. 1.—Probable rearrangement products.

possible products were necessary. *cis-* and *trans-*2-methyl-1-phenyl-1-butene (VIIIa and VIIIb) were prepared in poor yield by the Wittig reaction[6] of 2-butyltriphenylphosphonium iodide and benzaldehyde. Three olefins, 2-benzyl-1-butene (VI), 2-benzyl-2-butene (VIIab) and 3-methyl-1-phenyl-2-butene (X), were synthesized in high purity by the Cornforth procedure[7] from 1-chloro-2-butanone and benzylmagnesium chloride, 3-chloro-2-butanone and benzylmagnesium chloride, and from 3-chloro-4-phenyl-2-butanone and methylmagnesium chloride, respectively. 2-Methyl-4-phenyl-1-butene (IX) was prepared free from other isomers by the reaction of benzylmagnesium chloride with β-methallyl chloride.

Grignard reactions were used in the preparation of several alcohols: 2-benzyl-2-butanol (IV, S = H) from ethylmagnesium bromide and phenylacetone, 2-methyl-4-phenyl-2-butanol (V, S = H) from β-phenylethylmagnesium bromide and acetone, and 2-methyl-1-phenyl-1-butanol (XI, S = H) from 2-butylmagnesium bromide and benzaldehyde. Compound XI was included in the list of probable products because it could arise from addition of solvent to VIIIab.

A third type of product, an indane, could result from cyclization of a carbonium ion. The unrearranged carbonium ion from I could cyclize to 2,2-dimethylindane (XIII) while the carbonium ion from benzyl migration (III) could cyclize to 1,1-dimethylindane (XII). Compound XIII was prepared by cyclization of 2,2-dimethyl-3-phenylpropionic acid followed by Clemmensen reduction of the indanone.[8] Compound XII was prepared in good yield by treatment of V (S = H) with 85% sulfuric acid.[9]

The solvolyses in acetic acid and in formic acid were carried out on Ia at reflux temperatures, 118° and 101°, respectively. The deamination of Ib by sodium nitrite in acetic acid at 106° produced acetate esters as well as olefins. Formate esters were found as part of the product from the formolysis. Acetolysis yielded only olefin. Quantitative transformation of esters into alcohols without affecting the olefins was accomplished by treatment with lithium aluminum hydride. The olefin–alcohol mixtures were then analyzed by gas chromatography. Figure 1 shows the products to be expected from the rearrangements. Assignments of compounds to peaks were made by injecting a mixture of the unknown material with each of the pure known compounds. Enhancement of a peak then showed that the known compound had the same retention time as the peak. In this way, the assignments shown in Table I were established. The validity of the assignments was demonstrated for peaks 1, 2 and 4 by the identity of their infrared spectra with those of authentic pure samples. Peak 3 was analyzed qualitatively by ultraviolet and quantitatively by infrared spectroscopy, and peaks 4 and 5 were analyzed by quantitative ultraviolet spectroscopy. The results of the analyses are listed in Table I. The final percentages of methyl-migrated product probably are reliable to about 1% (see Experimental).

Control experiments to determine the behavior of the products under the reaction conditions were conducted. Selected samples of both benzyl-migrated and methyl-migrated products were subjected to the conditions of each of the three reactions. Some double bond position isomerization and interconversion of olefin and ester did occur. As expected, this was greatest for formolysis and least for deamination. There was no positive evi-

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TABLE I

ANALYSIS OF REARRANGEMENT PRODUCTS

Peak[a]	Rel. ret. time[a]	Cpd.	Acetolysis[b]	Formolysis[b]	Deamination[b]
Early	0.83	XIII	...	...	...
1	0.91	XII	...	5.93	...
2	1.00	VI	2.36	...	10.25
3	1.18	VIIab	42.78	10.16	21.94
		IX	1.64	...	...
4	1.29	VIIIa	14.21	6.74	...
5	1.45	VIIIb	28.13	12.92	2.65
		X	10.88	2.26	...
6	4.77	IV	...	19.11	46.21
7	6.96	V	...	5.19	18.95
8	8.9	XI	...	37.70	...
Methyl migration, %			87.48	86.63	81.05
Rel. migration apt.[c]			3.5	3.2	2.1

[a] Ucon-Polar column at 120°. [b] Mole per cent. [c] Corrected for statistical factor of 2; methyl/benzyl.

dence for carbon-skeleton isomerization and the pattern of the results makes such isomerization highly improbable. Completely unequivocal data are not easy to obtain, as some of the new peaks could contain material of either carbon skeleton. In none of the experiments was there a new peak attributable only to material of the other carbon skeleton. Therefore, it seems highly likely that our product analyses correctly reflect the relative rates of methyl and benzyl migration.

The migration aptitudes at the bottom of Table I show that methyl migrates better than benzyl under all the conditions we have studied. This result is in contrast to that obtained in migration to oxygen,[2] and suggests a fundamental difference in detailed mechanism between the two types of reaction. Clearly, the migrating group cannot possess carbonium-ion character in our reaction, as the benzyl is far more stable than the methyl carbonium ion. Benzyl is electron withdrawing relative to methyl in its inductive effect,[10] and this would decrease the electron density in the bond from the benzyl carbon to the quaternary carbon. These considerations suggest that the migrating group is still very close to the migration origin in the transition state so that the transition state resembles reactant. A similar conclusion was reached, on different grounds, for the methyl migration in the neophyl and neopentyl systems.[11]

The relative values of our migration aptitudes under different conditions seem reasonable. Our figure for deamination is similar in magnitude to that obtained by House[3] with an amino alcohol. Deaminations are known to be less selective than solvolytic carbonium-ion reactions.[12] If anything, the selectivity here is greater than expected. Conformational effects may play a role, though one would not expect them to be prominent with a primary migration terminus. The difference in product composition between formolysis and acetolysis is within probable experimental error, though again in the expected direction. Formolyses generally have lower activation energies than acetolyses[13] and therefore should show less selectivity.

Whether ionization and rearrangement are concerted cannot be decided definitely on present information. We believe they are, because there is no unrearranged product at all and the observed migration aptitudes depend upon the leaving group and (less convincingly) upon the reaction conditions. Combined rate and migration-aptitude studies on these and related compounds are planned so as to obtain more positive evidence on this point.

The two isomers of 2-methyl-1-phenyl-1-butene, VIIIa and VIIIb, were prepared in this work and isolated in the pure state by means of gas chromatography. Their properties are given in the Experimental. A tentative structural assignment may be based on the fact that the Wittig reaction gives VIIIa and VIIIb in a 1:3 ratio. This reaction is believed to give preferentially the more stable product *via* a four-center reaction,[14] and has previously been found in these laboratories to do so with 2-phenyl-2-butene.[11] Therefore VIIIb should be the isomer with phenyl and ethyl *trans* to each other. The other possible pair of *cis-trans* isomers, VIIa and VIIb, did not separate under the conditions used for gas-chromatographic analysis.

Experimental[15]

Methyl 2,2-Dimethyl-3-phenylpropionate.—Methyl isobutyrate (102 g., 1 mole) was added to 49.1 g. (1 mole) of a sodium hydride dispersion in mineral oil in one liter of tetrahydrofuran which had been purified according to Fieser.[16] The mixture was refluxed overnight, after which 126.6 g. (1 mole) of benzyl chloride in 300 ml. of tetrahydrofuran was added. The reaction mixture was refluxed for an additional 24 hours, the tetrahydrofuran was distilled off, and 300 ml. of petroleum ether (30–60°) was added. The mixture was washed with water, 4% acetic acid, water, dried over sodium sulfate, and the petroleum ether removed under vacuum. The residue was vacuum distilled to obtain 46.8 g. of benzyl chloride and 83.5 g. of product of b.p. 116–120° (14 mm.) (43% based on ester, 69% based on unrecovered benzyl chloride), n^{25}D 1.5014 (lit.[17] b.p. 102–103° (10 mm.), n^{25}D 1.4945).

2,2-Dimethyl-3-phenyl-1-propanol (Ic).—Methyl 2,2-dimethyl-3-phenylpropionate (4.8 g., 0.027 mole) was added to 1.0 g. of lithium aluminum hydride (0.027 mole) in 25 ml. of anhydrous ether with stirring. After 3 hours of refluxing, the mixture was decomposed by dropwise addition of 1.0 ml. of water, 1.5 ml. of 10% sodium hydroxide and 1.5 ml. of water. The solid settled, whereupon the supernatant liquid was removed and the solid washed with two portions of ether. All three solutions were combined and the ether was removed by distillation; 3.6 g. of a solid resulted which when sublimed gave 3.6 g. (81%) of white crystals, m.p. 33–35° (lit.[18] 34--35°). Other runs were distilled, b.p. 120–124° (14 mm.).

2,2-Dimethyl-3-phenyl-1-propyl *p*-Toluenesulfonate (Ia).—The tosylation was run *via* Marvel's method[19] using 91 g. of Ic (0.55 mole), 175 ml. of pyridine (2.22 moles) and 117 g. of *p*-toluenesulfonyl chloride (0.61 mole). The product was 138 g. (79% yield) of white crystals, m.p. 71.4–71.8°. *Anal.*

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Calcd. for $C_{18}H_{22}O_3S$: C, 67.89; H, 6.96. Found: C, 67.87, 68.42; H, 7.35, 6.98.

2,2 Dimethyl-3-phenyl-1-propylamine (Ib).—Methyl 2,2-dimethyl-3-phenylpropionate was saponified by refluxing overnight with 20% potassium hydroxide in methanol. The resulting acid had m.p. 57–57.7° after recrystallization from ethanol and petroleum ether (30–60°) (lit.[20] 56.5–58°). It was treated with thionyl chloride and subsequently aqueous ammonia[21] to yield an amide, m.p. 60–61° (lit.[20] 61–63°). 2,2-Dimethyl-3-phenylpropionamide (4.25 g., 0.024 mole) was treated with 2.7 g. of lithium aluminum hydride (0.072 mole) in refluxing tetrahydrofuran for 18 hours, the mixture was decomposed as in the preparation of Ic, and the supernatant liquid evaporated, leaving 1.60 g. of a yellow oil (41% yield). The *p*-bromobenzenesulfonamide had m.p. 106.4–107.4°. *Anal.* Calcd. for $C_{17}H_{20}BrNO_2S$: C, 53.40; H, 5.27. Found: C, 53.61; H, 5.33.

2-Benzyl-2-butanol (IV) was formed in the Grignard reaction of 0.5 mole of ethylmagnesium bromide and 67.0 g. of phenylacetone in anhydrous ether. The mixture was decomposed by the addition of saturated aqueous ammonium chloride followed by the usual workup. The product was vacuum distilled, b.p. 110–112° (14 mm.), resulting in 67.2 g. (82%) of product, n^{24}D 1.5097; phenylurethan, m.p. 82.3–83.7° (lit.[22] 83.5–84.0°).

2-Methyl 4-phenyl-2-butanol (V).—The procedure described above for 2-benzyl-2-butanol was followed. 2-Phenylethylmagnesium bromide (0.5 mole) and 35 g. of acetone produced 59.0 g. (72%) of V, n^{25}D 1.5080, b.p. 120–121° (13 mm.); phenylurethan, m.p. 139.1–140.1° (lit.[23] 143–144°).

2-Methyl 1-phenyl-1-butanol (XI).—2-Methyl-1-phenyl-1-butanol was prepared by the reaction of 0.3 mole of 2-butylmagnesium bromide and 31.8 g. of benzaldehyde in a 78% yield (38.3 g.), b.p. 108–124° (18 mm.). After oxidation with chromium trioxide, a 2,4-dinitrophenylhydrazone was prepared, m.p. 129–129.5° (lit.[24] for DNP of β-methylbutyrophenone, 128–129°).

2-Methyl-1-phenyl-1-butene (VIIIa and VIIIb). A. Wittig Reaction.[6]—2-Butyltriphenylphosphonium iodide (81.5 g., 0.182 mole) was added to 210 ml. of an ether solution of 0.162 mole of butyllithium (62.8% of the total alkalinity therein) which was cooled in a Dry Ice–acetone-bath. The deep red reaction mixture was refluxed for 4 hours, followed by addition of 19.6 g. of benzaldehyde (0.182 mole) in 50 ml. of anhydrous ether. The brown mixture was refluxed overnight, after which the ether was removed on a steam-bath. Petroleum ether (30–60°) was used to triturate the 147 g. of crude material. After evaporation of the petroleum ether, 5 g. of yellow oil remained, which was chromatographed on alumina in petroleum ether. The first few fractions contained 2.56 g. of colorless oil with the expected odor, 9.6% yield. A small amount was purified by microdistillation and analyzed. *Anal.* Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.03; H, 9.81. The presence of two compounds in a 1:3 ratio was shown by gas chromatography. These components were separated by gas chromatography and their ultraviolet and infrared spectra determined.

B. Thionyl Chloride–Pyridine Elimination.—To an ice-cooled mixture of 32.8 g. of IV (0.2 mole) and 50 ml. of dry pyridine was added with stirring 30 ml. of thionyl chloride (0.41 mole) in 50 ml. of pyridine. After stirring at 10° for 1 hour, the reaction mixture was poured over 50 g. of ice and 200 ml. of 10% hydrochloric acid. The product was extracted with two portions of chloroform, washed with dilute hydrochloric acid, water, aqueous sodium bicarbonate, and water. After drying over sodium sulfate, the chloroform was removed under vacuum and the product distilled. This resulted in 17.0 g. of a mixture of VI, VIIab and VIIIab (58% yield), b.p. 84–110° (24 mm.). The olefin mixture was subjected to gas chromatography, and the peaks corresponding to VIIIa and VIIIb were collected.

2-Methyl-4-phenyl-1-butene (IX).—To the Grignard reagent from 12.2 g. of magnesium (0.5 g.-atom) and 63.2 g. of benzyl chloride (0.5 mole) in 250 ml. of anhydrous ether was added 45.6 g. of β-methallyl chloride (0.5 mole) in 50 ml. of ether. The mixture was stirred at room temperature overnight and worked up by addition of 42 g. of sodium bicarbonate (0.5 mole), stirring 15 minutes, filtering through a bed of anhydrous magnesium sulfate, removing the ether under vacuum, and distilling the remainder. The product was 33.2 g. (45% yield) of colorless oil, b.p. 76–78° (12 mm.), n^{24}D 1.5040. The material was shown to be 99.8% pure IX by gas chromatography. *Anal.* Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.47; H, 9.57. The dibromide was an oil; the olefin was ozonized in methanol at −80° and worked up with trimethyl phosphite[25] followed by preparation of 2,4-dinitrophenylhydrazone, m.p. 127–128° (DNP of 4-phenyl-2-butanone,[26] m.p. 128.5–129°).

Chloro-2-butanones.—A mixture of 1- and 3-chloro-2-butanone was prepared by direct chlorination of 2-butanone,[27] and separated by fractional distillation into two fractions, b.p. 112–120° and 120–142°. The first half was redistilled through a 10-cm. Vigreux column with half of its volume of chlorobenzene (b.p. 132°). The fraction boiling at 112–124° was collected and the operation repeated. The ketone boiling at 115–120°, used in a following sequence of reactions, was ultimately demonstrated to be at least 99% 3-chloro-2-butanone. The second fraction was treated similarly, using 2-methoxyethanol (b.p. 124°). The ketone in this fraction, b.p. 135–138°, was subsequently shown to be at least 99% 1-chloro-2-butanone.

2-Benzyl-2-butene (VIIab). The Cornforth Sequence.[7]—The Grignard reagent from 94.9 g. of benzyl chloride (0.75 mole), 18 2 g. of magnesium (0.75 g.-atom) and 350 ml. of anhydrous ether was stirred vigorously at −80° and treated with 57.0 g. of 3-chloro-2-butanone (0.535 mole) in 50 ml. of ether at −80°. It was stirred 15 minutes, decomposed with 45 ml. of acetic acid in 50 ml. of ether, and worked up in the usual way. The fraction distilling at 125–130° (11 mm.) weighed 67.2 g. (65% yield). It was stirred vigorously with 0.375 mole of 1 *N* sodium hydroxide for 2 hours, separated, washed with water, dried, and distilled. The 2,3-epoxy-2-methyl-1-phenylbutane weighed 50.2 g. (92%), b.p. 91–103° (10 mm.).

To an ice-cooled solution of 78.7 g. of sodium iodide, 36 g. of sodium acetate and 12 ml. of water in 160 ml. of glacial acetic acid was added a small portion of zinc powder. Dropwise addition of 50.2 g. of the epoxide (0.31 mole) was begun and the rest of the zinc powder was added in portions until 78.7 g. was in. Both were all in within 10 minutes. The reaction mixture was stirred for 2 hours at 5–10°. It was poured into excess water, extracted with petroleum ether (30–60°), the extract washed with water, aqueous sodium bicarbonate, water, and dried with anhydrous sodium sulfate. After removal of the petroleum ether under vacuum, the residue was distilled, giving three fractions totaling 29.5 g. (65% yield), boiling at 73–87° (11 mm.). By gas chromatography, the fractions were shown to be 98.5%, 99.3% and 99.7% pure VIIab, (VIIa and VIIb were not separated under the conditions used), n^{24}D 1.5089. *Anal.* Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 88.69; H, 9.84. Good analyses could not be obtained on VIIab and VI (below), probably because of autoxidation in the time between preparation and analysis.

2-Benzyl-1-butene (VI).—The Cornforth sequence was used with benzylmagnesium chloride and 1-chloro-2-butanone as starting materials. 1-Chloro-2-benzyl-2-butanol was obtained in 54% yield, b.p. 110–131° (10 mm.). 1,2-Epoxy-2-benzylbutane was obtained in 84% yield, b.p. 92–105° (11 mm.). Compound VI was obtained in 38% yield, b.p. 74–79° (20 mm.), n^{25}D 1.5081. Gas chromatography showed it to be 99.2% pure. *Anal.* Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 88.75; H, 9.74. Ozonolysis[25] of the olefin was followed by preparation of a 2,4-dinitrophenylhydrazone, m.p. 145.8–146.7° (DNP of 1-phenyl-2-butanone, m.p.[28] 145.8–146.8°).

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3-Methyl-1-phenyl-2-butene (X).—3-Chloro-4-phenyl-2-butanone was prepared by the chlorination and decarboxylation of 2 moles of α-benzylacetoacetic ester[29] in 85% yield. No attempt was made to separate the isomers. The gas chromatogram of the final olefin showed that purity was about 95%. The Cornforth sequence was again followed, using methylmagnesium iodide and 3-chloro-4-phenyl-2-butanone. 3-Chloro-2-methyl-4-phenyl-2-butanol, b.p. 85–100° (1 mm.), was obtained in 77% yield. 2,3-Epoxy-2-methyl-4-phenylbutane, b.p. 68–82° (1 mm.), was obtained in 78% yield. Compound X was obtained in 55% yield, b.p. 99–103° (25 mm.), n^{27}D 1.5091. Gas chromatography showed 95.2% purity. A dibromide was prepared, m.p. 62.5–63.5° (lit.[30] 63–68°). The nitrosochloride had a m.p. 153.5–154° (lit.[30a,b] m.p. 147°, 154°).

1,1-Dimethylindane (XII).—This indane was prepared from 16.4 g. of V (S = H) by treatment with cold 85% sulfuric acid.[9] The product weighed 3.78 g. (26%) after distillation through a spinning band column at 71° (8 mm.), n^{24}D 1.5136 (lit.[9] b.p. 191°).

2,2-Dimethylindane (XIII).—Treatment of 10 g. of 2,2-dimethyl-3-phenylpropionic acid (0.057 mole) with 100 ml. of anhydrous hydrofluoric acid[8] for 1 day gave 8.5 g. (92.4%) of 2,2-dimethylindanone after chromatography on alumina, n^{25}D 1.5358. The semicarbazone had m.p. 206° (lit.[30f,31] 209–210° for one crystalline form). The ketone (5.0 g.) was reduced by the Clemmensen method[8] in 89% yield. Redistillation of the product through a spinning band column at 77–79° (16 mm.) gave 4.06 g. of XIII, n^{25}D 1.5068. *Anal.* Calcd. for $C_{11}H_{14}$: C, 90.35; H, 9.65. Found: C, 90.23; H, 9.50.

Reagents.—Anhydrous formic acid was prepared from Baker and Adamson 98% material by refluxing 24 hours with 10% by weight of boric anhydride,[32] and distilling the anhydrous acid from the solid.

Acetic acid was made anhydrous by the addition of 1.4% by weight of acetic anhydride to Mallinckrodt 99.7% analytical reagent glacial acetic acid 24 hours before use.

Other materials were analytical reagent, reagent or USP grade, dried before use.

Rearrangement in Acetic Acid.—A mixture of Ia (5.0 g.), sodium acetate (1.29 g.) and acetic acid (50 ml.) was refluxed (118°) for 76 hours, cooled, poured into excess water, extracted with petroleum ether (30–60°), and the extract washed with water, aqueous sodium bicarbonate and water. After drying over sodium sulfate, the petroleum ether was removed and the yellow oil chromatographed on alumina to remove any Ia present (usually about 0.3 g.). The 2 g. (87%, assuming it to be entirely olefin) of colorless oil was analyzed as described later.

Rearrangement in Formic Acid.—Compound Ia (5.0 g.), sodium formate (1.07 g.), and formic acid (50 ml.) were refluxed (101°) for 44 hours. The initially homogeneous mixture became heterogeneous. The above purification was followed, except that the crude oil was treated with lithium aluminum hydride in ether and was not chromatographed. The product usually weighed nearly 2.4 g. (about 90%, assuming 62% alcohol and 38% olefin).

Rearrangement of Ib.—A solution of Ib (1.42 g.) in acetic acid (15 ml.) was heated to 106° and held there while 2.4 g. of sodium nitrite was added in portions in the course of a half-hour. After 12 hours of heating at the same temperature, the mixture was cooled and treated in the same way as the formolysis product.

Stability of Rearrangement Products under Reaction Conditions. A. Acetolysis.—A solution of VIIab (1.0 ml.) in 50 ml. of acetic acid containing 1.29 g. of sodium acetate was refluxed for 90 hours. The gas chromatogram of the product showed 89.9% unrearranged olefin and three additional peaks which could be accounted for by double bond migration. No peaks explainable only by skeletal migration were observed.

Compound X (1.0 ml.) was refluxed with acetic acid (20 ml.) and sodium acetate (0.32 g.) for 72 hours. Gas chromatography of the product showed two peaks with retention times the same as IX and X. No other peaks were present.

B. Formolysis.—Compound VIIab (2.0 g.), formic acid (50 ml.) and sodium formate (0.5 g.) were refluxed for 41 hours. Following the usual formolysis workup, the gas chromatogram showed extensive double bond migration and ester formation, but no evidence for skeletal rearrangement.

Compound IX (1.0 g.), formic acid (25 ml.) and sodium formate (0.25 g.) were refluxed for 41 hours. The product was 95% V with a little XII present. No skeletal rearrangement was observed.

D. Deamination.—2-Benzyl-2-butyl acetate (2.0 g.) and acetic acid (20 ml.) were heated to near reflux and treated in the course of 30 minutes with sodium nitrite (3.05 g.). After refluxing for 12 hours, the reaction mixture was worked up in the same manner as the acetolysis. Gas chromatography showed no peaks explainable only by the other carbon skeleton. Olefin formation appeared to be less than 5%.

2-Methyl-4-phenyl-2-butyl acetate (2.0 g.) and acetic acid (20 ml.) were given the same treatment. The resulting material also showed no evidence of skeletal rearrangement. Again, almost no olefin was formed.

Gas Chromatography.—Gas chromatographic methods have been described in an earlier paper.[11] The columns used were Carbowax 1500 (Union Carbide Co., a polyethylene glycol of average molecular weight 1500), Reoplex 400 (Wilkins Instrument and Research Inc., a glycol–adipate polyester of unknown molecular weight), Apiezon L (a high molecular weight hydrocarbon grease) all for separating olefins; and Ucon Polar (Wilkins Instrument and Research, Inc., a polypropylene glycol of unstated molecular weight) for alcohols and olefins. All of the columns were 6 mm. outside diameter except two Reoplex 400 columns, one 9 mm. and the other 12 mm. outside diameter, which were used for separating and collecting the olefins. Temperatures for analysis of olefins were around 100° and for the alcohols and olefins, about 120° with flow rates of usually 50 to 100 ml. per minute.

Compounds were concluded to have the same retention times if injection of a mixture of the two into the gas stream produced a single peak. This was the sole basis for assigning the identity of alcohol peaks. In the case of indanes and olefins, the infrared and ultraviolet spectra of the collected peaks were obtained to confirm the identifications.

Infrared Analysis.—Quantitative analysis by infrared spectroscopy was accomplished by means of a Perkin–Elmer model 21 double beam infrared spectrometer operated at a speed of about 3 μ per hour. A cell with sodium chloride

TABLE II

ANALYSIS OF PEAK 3 BY INFRARED SPECTROSCOPY

Peak ratio used	Acetolysis[a]	Formolysis[a]
5.96μ/ 6.04 μ	96.5	96.3[b]
11.95 μ/11.25 μ	95.4	100
12.85 μ/11.25 μ	97.0	100
Average	96.3 ± 0.6	100

[a] % VIIab present. [b] Error probably due to small amount of peak 4 olefin present.

TABLE III

ULTRAVIOLET MAXIMA

Compound	λ_{max}, mμ	ϵ_{max}	Compound	λ_{max}, mμ	ϵ_{max}
VI	258	275	X	261	417
VIIab	259	308	Peak 3[a]	259	285
VIIIa	245	13,300	Peak 4[a]	245	13,200
VIIIb	246	14,600	Peak 5[a]	246	10,600
IX	261	226	Peak 5[b]	245	12,500

[a] From acetolysis. [b] From from formolysis.

TABLE IV

ANALYSIS BY ULTRAVIOLET SPECTROSCOPY

Compound	Peak number 4[a], %	5[a], %	5[b], %
VIIIa	99	..	..
VIIIb	..	72.1	85.1

[a] Peak from acetolysis. [b] Peak from formolysis.

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windows and a path length of 0.06 mm. was filled with mixtures of olefins of known ratios. The relative intensities of peaks were used to make a graph against which the unknown was compared.

Ultraviolet Analysis.—Quantitative analysis by ultraviolet spectroscopy utilized a Cary double beam recording spectrophotometer. At least four samples were used for each recorded value. The following equation was used to obtain the composition of the unknown mixture

$$\epsilon_{\text{exp}} = \epsilon_1 X_1 + \epsilon_2(1 - X_1)$$

in which ϵ_{exp} is the observed extinction coefficient, ϵ_1 and ϵ_2 are the extinction coefficients of the pure compounds at the wave length used, and X_1 the mole fraction of component 1. The ϵ used for VIII at 245 mμ was 200.

Precision of Results.—Limits of error are somewhat difficult to assess, as several analytical methods enter in. Analyses by gas chromatography were done on eight acetolysis products. There was considerable variation in percentages of individual components, presumably due to differing amounts of double-bond-position isomerization for different reaction times. Five of these (including the quoted run) done for reaction times of 57–76 hours averaged 87.56% of methyl-migrated product with an average deviation of 0.24%. The percentages from Tables III and V (determined for the quoted run) were used to find the contributions of each component in the two two-component peaks. Inclusion of the other three runs (36, 44 and 97 hours) raised the average to 88.46 and the average deviation to 1.12%. Application of the percentages in Tables II and IV to these data obtained under different conditions is questionable, however. Unless undetected systematic errors enter in, our percentage of methyl-migrated material in acetolysis seems easily good within 1%. The formolysis and deamination reactions were not studied so extensively, but there seems no reason for suspecting them to be of notably poorer precision.

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Unpaired Electron Distribution in π-Systems

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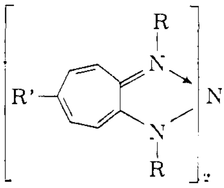
Electron spin densities have been mapped by n.m.r. contact shifts in a series of aryl groups attached by the azo linkage to the γ-position of nickel aminotroponeimineates, and the results compared with those obtained previously for the analogous substituents attached to the nitrogen atoms of aminotroponeimines. Although observed spin density distributions for a given substituent attached at the two points are similar, the differences suggest that the conjugated system of the γ-arylazo group is extended into the region of the seven-membered ring, whereas the substituent at the nitrogen atom is essentially isolated from the seven-membered ring. In addition, methyl contact shifts in paramagnetic aromatic systems, which arise primarily from effects of hyperconjugation, were found to depend markedly on position of methyl substitution. Similarly, direct evidence in the form of F^{19} contact shifts is presented for participation by fluorine in conjugation in fluoroaromatics.

We have reported previously that the proton resonances in the n.m.r. spectra of the paramagnetic nickel(II) chelates of aminotroponeimines (I) are shifted from the positions observed for the corresponding protons in the free ligands (II) by as much as 7000–10,000 c.p.s. at 60 Mc./sec.[1–4] These shifts (arising from isotropic hyperfine contact interactions[5]) are due to the enhanced or diminished magnetic field at the proton resulting from the presence of a fractional unpaired electron on carbon. This unpaired electron arises from delocalization of an unpaired electron which is produced at the nitrogen atom through dπ–pπ bonding with nickel. This finding provides an approach utilizing n.m.r. for (1) measurement of the unpaired electron distributions in π-electron systems,[1–4] (2) establishing the relative ability of different functional groups to delocalize an odd electron (conjugating ability)[2,6] and (3) obtaining information on both C–H and C–F bonding on sp^2- and sp^3-carbon atoms.[4,6]



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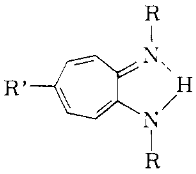

II

The present paper reports unpaired electron distributions in a number of aromatic substituents joined by the azo function to the γ-position of a nickel(II) aminotroponeimineate. This study provides further information on C–H and C–F bonding in sp^2 and C–H bonding in sp^3 situations and permits correlation of these new results with those of our prior findings obtained for the same substituents attached to the nitrogen atoms of the aminotroponeimines.

Introduction

The use of aminotroponeimines as probes for providing information regarding electronic structure of π-systems is markedly facilitated by the chemical and physical properties of these compounds. A broad spectrum of N-substituted derivatives can be obtained by reaction of the tetrafluorocycloheptadienes with appropriately substituted primary amines.[7] In addition, the aminoimines as a class show aromatic character and undergo attack by certain electrophilic reagents at the γ-position. The γ-arylazo derivatives reported in this paper were prepared by action of the appropriate diazonium fluoroborates on the aminoimine. These compounds and their zinc and nickel chelates have sufficient solubility in deuteriochloroform or

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