Friedel–Crafts Reaction of 3,4,4-Trimethybutyrolactone and Benzene

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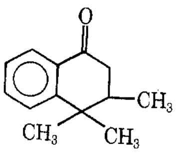
The Friedel-Crafts reaction of 3,4,4-trimethylbutyrolactone (**2**) and benzene in the presence of greater than 2 equiv of aluminum chloride has been found to give three ketones, 3,4,4-trimethyl-1-tetralone (**1**), 3,3,4-trimethyl-1-tetralone (**3**), and 3,4-dimethyl-1-phenyl-1-pentanone (**4**). With 2 equiv of aluminum chloride, **1** is the only neutral product, and, with less than 2 equiv, 4-phenyl-3,4-dimethylpentanoic acid (**5**) is obtained. The use of benzene-d_6 in these reactions leads to incorporation of deuterium in the aliphatic portion of the molecule in the ketones but not in the acid. A mechanism is proposed which suggests that, in the presence of 1 equiv of aluminum chloride, **2** is converted to a tertiary carbonium ion which with excess Lewis acid is transformed into an acyl carbonium ion and thence to 3,4-dimethyl-1-phenyl-3-penten-1-one (**10**). 3,4-Dimethyl-1-phenyl-2-penten-1-one was prepared and with 3 equiv of aluminum chloride gives **1** and **4**. A detailed mechanism is suggested for these reactions.

Some time ago, in an effort to prepare 3,4,4-trimethyl-1-tetralone (1), we reported the reaction of 3,4,4-trimethylbutyrolactone (2) and benzene with excess aluminum chloride.[2] Although reactions of this type had been reported by others and seemed to proceed smoothly to give a single product,[3] we obtained a mixture consisting of 53% **1**, 41% 3,3,4-trimethyl-1-tetralone (**3**), and 6% of a third compound of unknown structure.[2] On the basis of analytical and spectral data, this compound appeared to be isomeric with **1** and **3**, but it was none of the several obvious products which could be obtained from a carbonium ion intermediate derived from **2**. Since there were only very small amounts of this compound obtainable and the instrumental tools available to us at the time were very limited, the approach to the elucidation of the structure was the synthesis of various compounds which appeared to be logical products of the reaction.[2,4]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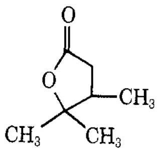
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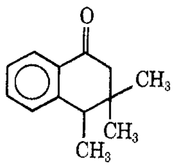
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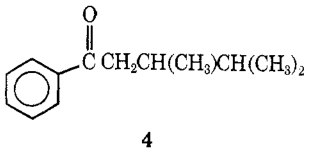
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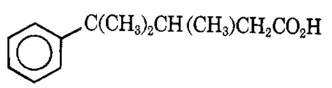
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In an effort to gain further insight into the nature of this compound, it was subjected to mass spectrometry;[5] however, rather than the expected parent ion at m/e 188, this compound showed a peak at m/e 190. A first-order analysis of the mass spectrum clearly indicated that it was 3,4-dimethyl-1-phenylopentan-1-one (**4**). The mass spectral data (see Table I) may be interpreted as follows: the base peak at m/e 105 corresponds to an acylium ion ($C_6H_5C{\equiv}O^+$), while the peak at m/e 120 is the result of a McLafferty rearrangement. The peak at m/e 147 is the result of the loss of the isopropyl group, while the one at m/e 77 arises from a phenyl ion. The nmr data for this compound were also in agreement with the assigned structure (see Experimental Section) which was confirmed by the synthesis of **4** from 3,4-dimethylpentanoic acid[6] and benzene.

TABLE I

MASS SPECTRAL DATA[a]

Compd	m$^+$ (rel abundance)	m/e	m/e	m/e	m/e
1	188 (100)	173 (97)	145 (78)	131 (61)	
3	188 (97)	145 (47)	132 (100)	104 (92)	
4	190 (40)	147 (88)	120 (98)	105 (100)	77 (98)

[a] Principal peaks only.

Although reductions under relatively mild Friedel–Crafts conditions have been reported by Fuson[7] and under more vigorous conditions by Dippy,[8] very little is known concerning the course of these reactions. In an effort to gain some insight into the mechanism of the reduction, as well as the course of the alkylation–acylation reaction of **2** with benzene, the Friedel–Crafts reaction was carried out using benzene-d_6. The same mixture of ketones was obtained; however, all three compounds exhibited very high and specific incorporation of deuterium, as disclosed by their nmr spectra. In the case of **1**, the C-3 methyl doublet at 0.99 ppm was now a singlet and the three-proton multiplet at 2.46 ppm had become an AB quartet with a coupling constant (17 Hz) indicative of nonequivalent geminal protons. Thus, there was exclusive and nearly 100% deuterium incorporation at C-3. In **3**, the methyl doublet at 1.26 ppm had become a singlet and the signal due to the benzylic proton had disappeared, indicating deuterium incorporation at this position. The nmr spectrum of deuterated **4** showed only a broadened

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[1] Abstracted from the M.S. Thesis of J. J. Starnes, Clemson University, May 1971.

[2] J. W. Huffman and T. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).

[3] (a) R. T. Arnold, J. S. Buckley, and J. Richter, *J. Amer. Chem. Soc.*, **69**, 2322 (1947); (b) W. L. Mosby, *ibid.*, **74**, 2546 (1952); (c) W. E. Truce and C. E. Olson, *ibid.*, **74**, 4721 (1952).

[4] In addition to the compounds described in ref 2, two other ketones, 3- and 4-isopropyl-1-tetralone, have been synthesized by unexceptional methods.[1]

[5] The authors would like to thank the Research Triangle Institute for Mass Spectrometry, Research Triangle Park, N. C., for carrying out this determination.

[6] R. C. Haston and A. H. Agett, *J. Org. Chem.*, **6**, 132 (1941). Our synthesis of this compound is somewhat different from that reported by these workers and is described in detail in the Experimental Section.

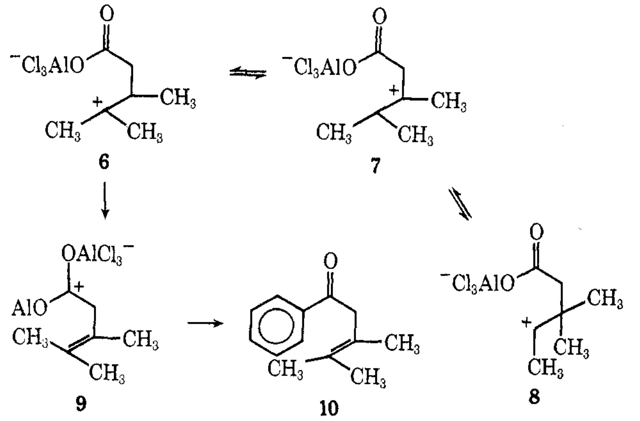
[7] (a) R. C. Fuson, L. L. Alexander, and A. L. Jacoby, *J. Amer. Chem. Soc.*, **57**, 2208 (1935); (b) R. C. Fuson and L. L. Alexander, *ibid.*, **58**, 1745 (1936).

[8] (a) J. F. J. Dippy and A. L. L. Paulluel, *J. Chem. Soc.*, 1415 (1951); (b) J. F. J. Dippy and J. T. Young, *ibid.*, 3919 (1955).

methyl singlet at 0.89 ppm and an AB quartet (J = 15 Hz) at 2.80 ppm, indicating the incorporation of two deuterium atoms into the alkyl side chain at C-3 and C-4.[9]

In view of the fact that **1** is stable to further reaction with excess (3.18 mol) aluminum chloride in benzene and the apparently generally accepted mechanism for the reaction of lactones under Friedel–Crafts conditions,[2,3c] these results were most surprising. The Truce mechanism suggests alkylation as a first step to give a γ-arylbutyric acid, in this case **5**, as the initial product, with cyclization to the tetralone as a subsequent step.[3c] If alkylation to **5** were occurring first, then it becomes very difficult to reconcile the formation of **4**. Also, the very high incorporation of deuterium into **1** and the formation of **3** would necessitate the formation of an equilibrating mixture of carbonium ions (**6**, **7**, and **8**) which would have to undergo deuterium exchange with the solvent.

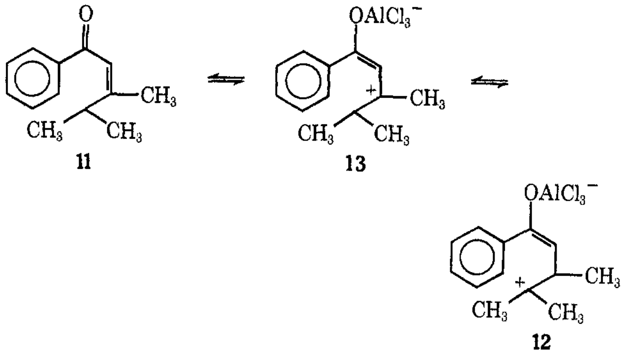
This mechanism is unsatisfactory for two reasons. First, no trace of the indanone derived from **7** could be detected; and second, the tertiary carbonium ion (**6**) should be sufficiently more stable than either **7** or **8** that the bulk of the product should arise from this intermediate.



Since it has been previously noted that the reaction of **2** with benzene gave **5** in reasonable yield with 1 equiv of aluminum chloride,[2] this reaction was repeated using benzene-d_6. *The acid in this manner was free of isomers and had no deuterium in the alkyl side chain.* These results indicate that, with 1 equiv of aluminum chloride, carbonium ion **6** is formed, and, without rearrangement, alkylates the substrate. Further, it is apparent that, since no deuterium is incorporated into **5**, the ketones formed with excess aluminum chloride must arise by way of a different mechanism.

Since the molar ratio of aluminum chloride to lactone appears to profoundly affect the course of this reaction, it was repeated using 2.0 and 2.6 equiv of aluminum chloride. With 2.0 equiv there was obtained only 3,4,4-trimethyl-1-tetralone (**1**) and, when the reaction was carried out in benzene-d_6, deuterium was incorporated at C-3 as described above. With 2.6 equiv of aluminum chloride ketones **3** and **4** were also formed, but in smaller amounts than when 3 or more equiv were used.

A consideration of the reactions of lactones with superacids[10] indicates that, in the presence of more than 1 equiv of aluminum chloride, carbonium ion **6** is probably converted to the acyl carbonium ion derived from 3,4-dimethyl-3-pentenoic acid (**9**). This carbonium ion can then react with benzene to give an unsaturated ketone (**10**) which, under the influence of acid, either hydrogen chloride formed *in situ*, or excess aluminum chloride would cyclize to the tetralones or undergo reduction to **4**.



In order to check this hypothesis, 3,4-dimethyl-1-phenyl-2-penten-1-one (**11**) was synthesized by the reaction of the appropriate acid chloride and benzene. This ketone is considerably more accessible than **10** and on acid treatment would be expected to be converted to a similar carbonium ion (**12**). This expectation was borne out when **11** was treated with 3.2 equiv of aluminum chloride to give a mixture of 6% reduction product (**4**) and 94% **1**. However, when the reaction was carried out in benzene-d_6, little, if any, deuterium incorporation was observed. Surprisingly, the rearranged tetralone (**3**) was not obtained in these reactions. Insufficient **4** was obtained from the experiments in benzene-d_6 to permit its isolation and characterization. Although the failure to obtain deuterium incorporation in the cyclization of **11** was unexpected, it is easily explained if the intramolecular hydride shift from **13** to **12** and the cyclization of **12** are fast compared to exchange with solvent, which would lead to deuteration.

The reactions of **2** with benzene and excess aluminum chloride may all be interpreted in terms of the mechanism outlined in Scheme I. This mechanism accounts well for all the observed results, and in particular the failure to obtain **3** in the cyclization of **11**. In the presence of excess aluminum chloride, intermediate **14** may be stabilized, thus permitting significant amounts of ketone **3** to be formed by way of the intermediates shown. The exact mechanism of the reduction of **11** to **4** is not clear. Although the derived hydrogens are obtained from benzene, biphenyl is not a product of this reaction.

Whether this type of multiple reaction path is operative in the Friedel–Crafts reaction of simple lactones is not known, but it is quite certain that in this case, at least, the Truce mechanism[3c] is excluded. In the course of this work, the mass spectra of both tetralones (**1** and **3**) were determined, and these are included in Table I.

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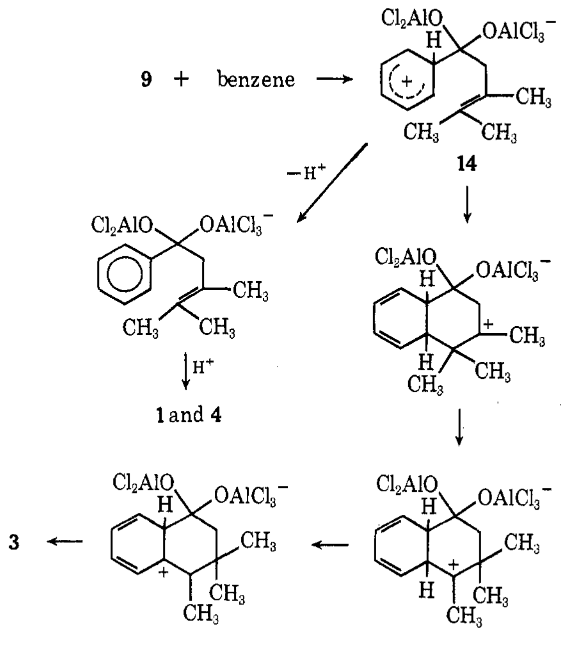
[9] In all these compounds, there was, of course, complete deuteration of the aromatic ring.

[10] G. A. Olah and A. T. Ku, *J. Org. Chem.*, **35**, 3916 (1970).

Scheme I



Experimental Section[11]

Reaction of 3,4,4-Trimethylbutyrolactone and Benzene.—This reaction was carried out, and the mixture of ketones was isolated by the method reported earlier.[2] Separation of the mixtures of isometric ketones was accomplished by preparative glc to give **3,4,4-trimethyl-1-tetralone** (**1**) which shows nmr signals at 0.99 (d, J = 7 Hz, CH_3CH), 1.22 (s, 3 H, CH_3), 1.37 (s, 3 H), 2.46 (m, 3 H, CH_2CH), 7.36 (m, 3 H, ArH), 7.92 ppm (m, 1 H, ArH); **3,3,4-trimethyl-1-tetralone** (**3**), nmr 1.01 (s, 6 H, CH_3), 1.26 (d, J = 7 Hz, 3 H, CH_3CH), 2.74 (m, 3 H, CH_2 and CH), 7.40 (m, 3 H, ArH), 7.92 ppm (m, 1 H, ArH); and **3,4-dimethyl-1-phenylpentan-1-one** (**4**), nmr 0.92 (overlapping d, J = 7 Hz, 9 H, CH_3CH), 1.81 (m, 2 H, CHCH), 2.82 (m, 2 H, CH_2), 7.45 (m, 3 H, ArH), 7.93 ppm (m, 2 H, ArH).

When the reaction was carried out in benzene-d_6 and the compounds were isolated as described above, the deuterium-decoupled nmr spectra of the ketones are, for **3,4,4-trimethyl-1-tetralone**, 1.04 (s, 3 H, CH_3), 1.32 (s, 3 H, CH_3), 1.37 (s, 3 H, CH_3), 2.65 ppm (AB, J = 7 Hz, CH_2); **3,3,4-trimethyl-1-tetralone**, 0.99 (s, 6 H, CH_3), 1.26 (s, 3 H, CH_3), 2.48 (AB, J = 17 Hz, CH_2); and **3,4-dimethyl-1-phenylpentan-1-one**, 0.89 (br s, 9 H, CH_3CD), 2.80 (AB, J = 15 Hz, CH_2).

The use of limited quantities of aluminum chloride gave as reported previously **3,4-dimethyl-4-phenylpentanoic acid** (**5**): mp 64–67° (lit. mp 74–75°);[2] nmr 0.90 (d, J = 6 Hz, 3 H, CH_3CH), 1.28 (s, 6 H, CH_3), 2.16 (m, 3 H, CH_2CH), 7.28 ppm (br s, 5 H, ArH). When the alkylation was carried out in benzene-d_6 the nmr was identical with the exception of the loss of the signal at 7.28 ppm. The methyl ester of the once recrystallized acid was homogenous to glc.

The results of several reactions of this type are summarized in Table II.

Ethyl 3,4-Dimethyl-2-pentenoate.—To a stirred slurry of 4.8 g of 50% sodium hydride in 190 ml of 1,2-dimethoxyethane cooled in an ice bath and under a nitrogen atmosphere was added dropwise 22.4 g of triethyl phosphonoacetate. The mixture was stirred for 1 hr and 8.6 g of methyl isopropyl ketone were then added dropwise. The reaction mixture was heated at 60° for 24 hr, cooled to room temperature, diluted with water, and extracted with ether. The ethereal extracts were dried and the solvent was evaporated. Distillation afforded 9.8 g (63%) of unsaturated ester: bp 185–187° (lit.[12] 189–191°); nmr 1.2 (m, 9 H, CH_3CH and CH_3CH_2), 2.13 (d, J = 1 Hz, 3 H, CH_3), 2.15 (m, 1 H, CH), 4.12 (q, 2 H, CH_3CH_2), 5.16 ppm (br s, 1 H, vinyl CH); ir 3.42, 5.82, 6.08 μ.

Table II

Products from the Reaction of 3,4,4-Trimethylbutyrolactone and Benzene

Run	Solvent[b]	2, mmol	$AlCl_3$, mmol	5, %[a]	1, %[a]	3, %[a]	4, %[a]
1	Benzene	120	410	0	41	32	5
2	Benzene	15.6	31.5	0	60	0	0
3	Benzene	15.6	41.3	0	57	13	1
4	Benzene-d_6	20.3	69.3	0	43	34	5
5	Benzene-d_6	4.20	8.30	0	49	0	0
6	Benzene	5.90	7.60	57[c]	0	0	0
7	Benzene-d_6	1.56	1.88	87	0	0	0
8[d]	Benzene	120	410	0	41	32	5
9[d]	Benzene	150	120	60	18	0	0
10[e]	Benzene	0	8.22	0	100	0	0

[a] Reported in per cent based on lactone. [b] All reactions were carried out at 15° for 1 hr and then heated at reflux for 2 hr. [c] After two recrystallizations. [d] Reference 2. [e] Attempted isomerization of 2.18 mmol of 1. Carried out at reflux for 24 hr.

3,4-Dimethyl-2-pentenoic Acid.—To 5.0 g of ethyl 3,4-dimethyl-2-pentenoate were added 50 ml of 20% potassium hydroxide and 50 ml of ethanol. The mixture was heated at reflux for 12 hr and the acid was isolated in the usual manner and distilled to give 2.6 g (63%): bp 73–76° (0.5 mm) [lit.[13] 83–94° (1.5 mm)]; nmr 1.09 (d, J = 7 Hz, 6 H, CH_3CH), 2.17 (s, 3 H, CH_3), 3.4 (m, 1 H, CH), 5.75 ppm (s, 1 H, vinyl CH).

3,4-Dimethylpentanoic Acid.—This compound was prepared by hydrolysis of ethyl 3,4-dimethylpentanoate,[14] which was in turn obtained by reduction of the unsaturated ester described above. From 9.70 g of pentenoate 4.70 g (60%) of saturated acid, bp 209–210° (lit.[6] 210–214°), were obtained: nmr 0.85 (overlapping d's, 9 H, CH_3CH), 1.55 (m, 2 H, CHCH), 2.22 ppm (m, 2 H, CH_2).

3,4-Dimethyl-1-phenylpentan-1-one (4).—To 3.0 g of 3,4-dimethylpentanoic acid were added 13.0 g of thionyl chloride and the mixture was heated on the steam bath for 2 hr. The excess thionyl chloride was removed, leaving a residue of 3.2 g of acid chloride, which was added to a chilled, stirred slurry of 5.0 g of anhydrous aluminum chloride in 100 ml of dry benzene. The slurry was stirred in an ice bath for 1 hr and heated under reflux for 2 hr. The solution was cooled to room temperature and poured into a slurry of ice and hydrochloric acid. The aqueous layer was separated and extracted with ether. The organic fractions were combined, washed with 5% sodium hydroxide and water, and dried. The solvent was removed under reduced pressure and the resulting oil was distilled, giving 3.1 g (68%) of ketone, bp 85° (0.25 mm). The infrared and nmr spectra were identical with those of the compound obtained from the Friedel–Crafts reaction of 3,4,4-trimethylbutyrolactone and benzene.

3,4-Dimethyl-1-phenyl-2-penten-1-one (11).—To a solution of 4.0 g of 3,4-dimethyl-2-pentenoic acid in 50 ml of benzene was added 7.5 ml of oxalyl chloride, during which time a vigorous reaction took place. The solution was stirred at room temperature for 2 hr and the excess oxalyl chloride and benzene were distilled off. The product was dissolved in 25 ml of benzene and the benzene was again removed, leaving 4.5 g of crude acid chloride. This material was added to a stirred slurry of 4.7 g of aluminum chloride in 100 ml of benzene cooled in an ice bath. The reaction mixture was stirred at ice bath temperature for 0.5 hr and at room temperature for 24 hr and then heated to 60° for 25 min. The solution was cooled to room temperature and poured into a slurry of ice and concentrated hydrochloric acid. The aqueous layer was drawn off and extracted with ether. The organic extracts were combined, washed with 5% sodium hydroxide and water, and dried. The solvent was removed at reduced

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[11] All melting points were determined on a Kofler hot stage apparatus and are uncorrected. Infrared spectra were taken as potassium bromide disks or liquid films on sodium chloride plates using a Perkin-Elmer Model 137 spectrophotometer and are reported in microns. Nuclear magnetic resonance spectra were obtained in deuteriochloroform using a Varian Associates A-60 nuclear magnetic resonance spectrometer. All spectra are reported in parts per million relative to internal tetramethylsilane (δ). Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn. Gas–liquid chromatography was carried out on an F and M Model 810 analytical gas chromatograph using helium as the carrier gas at a flow rate of 35 ml/min through a 10 ft × 0.125 in. copper column of 10% QF1 on 'HP' Chromosorb W (80–100 mesh).

[12] R. Fittig and O. Kraft, *Justus Liebigs Ann. Chem.*, **208**, 71 (1881).

[13] L. I. Smith, W. L. Kohlhase, and R. J. Brotherton, *J. Amer. Chem. Soc.*, **78**, 2533 (1956).

[14] P. A. Levene and R. E. Marker, *J. Biol. Chem.*, **111**, 308 (1935).

pressure, yielding 4.02 g of crude product, which was dissolved in hexane and chromatographed on Merck alumina. Elution with hexane gave 1.20 g (20%) of pentenone: bp 99-101° (0.32 mm); nmr 1.21 (d, J = 6 Hz, CH_3CH), 2.10 (br s, 3 H, CH_3), 2.15 (m, 1 H, CH), 6.49 (br s, 1 H, vinyl CH), 7.13 (m, 3 H, ArH), 7.62 ppm (m, 2 H, ArH); ir 3.35, 5.95, 6.25 μ. This material could not be obtained completely homogenous to glc and was characterized by mass spectrometry, molecular ion at m/e 188.

Cyclization of 3,4-Dimethyl-1-phenyl-2-penten-1-one. A.—A solution of 0.10 g (0.53 mmol) of 3,4-dimethyl-1-phenyl-2-penten-1-one in 1.0 ml of dry benzene was added to a chilled slurry of 0.227 g (1.7 mmol) of aluminum chloride in 4.0 ml of dry benzene. The reaction mixture was stirred at ice bath temperature for 1 hr and then heated at reflux for 2 hr. Isolation of the product in the manner previously described gave 0.095 g (95%) of a viscous oil which was shown by glc to consist of 3,4-dimethyl-1-phenylpentan-1-one (4) and 3,3,4-trimethyl-1-tetralone (1) in a ratio of 6:94, respectively.

B.—A solution of 0.4 g (2.1 mmol) of 3,4-dimethyl-1-phenyl-2-penten-1-one in 5.0 ml of benzene-d_6 was added to a chilled, stirred slurry of 0.64 g of aluminum chloride in 15 ml of benzene-d_6. The reaction was carried out and the product was isolated as described above to give 0.36 g (90%) of viscous oil. The crude product was dissolved in benzene and chromatographed on alumina. Ether eluted the product, which was shown to be homogenous by vapor phase chromatography and the nuclear magnetic resonance and infrared spectra of which were identical with those of 3,4,4-trimethyl-1-tetralone obtained from the Friedel-Crafts reaction of 3,4,4-trimethylbutyrolactone and benzene.

Registry No.—**1**, 2981-99-9; **2**, 2981-96-6; **3**, 2982-01-6; **4**, 32557-33-8; **5**, 2977-36-8; **11**, 32557-35-0; benzene, 71-43-2; ethyl 3,4-dimethyl-2-pentenoate, 6570-79-2; 3,4-dimethyl-2-pentenoic acid, 32557-37-2; 3,4-dimethylpentanoic acid, 3302-06-5.

Interaction of Carbanions with Azobenzene and Related Compounds[1a,b]

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Reaction of alkali salts of active hydrogen compounds with azobenzene follow three general pathways: (1) addition to afford substituted hydrazobenzenes; (2) oxidation-reduction to often give dimer of the active hydrogen compound; and (3) addition-elimination to afford anils. In contrast to earlier work, the current study has ascertained that the most general pathway for such reactions is addition. Thus, the synthesis of 21 new hydrazobenzenes, prepared by three different methods, is reported. The addition reactions, apparently kinetically controlled in ammonia, proceed *via* intermediate monoanions of the hydrazobenzenes as evidenced by a trapping experiment with benzoyl chloride. Redox reactions have currently been observed only in two rather special cases: 9,10-dipotassioacenaphthene with azobenzene, and lithiodiphenylmethane with a highly conjugated azo compound. Interaction of either the monoalkali or geminal dialkali salts of phenylacetonitrile with azobenzene has given an interesting cyanoenamine, presumably *via* a novel "base-catalyzed" deamination. Similar deaminations have been observed with other systems, including some hydrazobenzenes, to afford anils. Certain of the latter conversions are rationalized by considering the thermodynamic and kinetic acidities of the hydrazobenzenes.

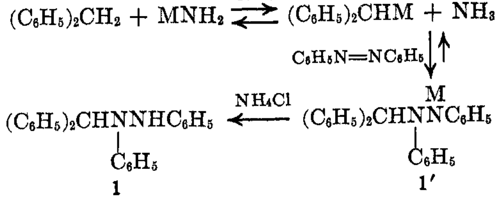
Previously, it has been shown that carbanions usually transfer an electron to the azo linkage of aromatic azo compounds in solutions of ether[2a] or dimethyl sulfoxide,[2b] resulting in reduction of the nitrogen-nitrogen double bond and, sometimes, in isolation of the oxidative dimer of the carbanion.[2a] Only rarely, though, have such reactions resulted in ionic addition of carbanions across the azo linkage to give substituted hydrazo compounds. Thus, the highly reactive phenylpotassium,[2a] phenylcalcium iodide,[2a] and phenyllithium[3] have been observed to so add to azobenzene to afford 1,1,3-triphenylhydrazine in low yields.

Our initial interest in azobenzene and related compounds stemmed from their potential use as oxidants in the dimerization of carbanions in liquid ammonia.[4] Instead of the expected oxidation-reduction reactions, though, these interactions have been found to constitute a presumably general synthesis of arylated hydrazines. This paper describes the three methods developed to effect such syntheses and illustrates not only interesting solvent and temperature effects, but also discusses novel base-catalyzed deaminations of certain of the hydrazine products.

Results and Discussion

Initial efforts were directed toward interacting the monoalkali salts of diphenylmethane with azobenzene in liquid ammonia. Surprisingly, aside from some recovered starting materials, only hydrazine **1**, the product arising from addition across the azo linkage, was isolated in variable yields (Scheme I); the expected dimeric product, 1,1,2,2-tetraphenylethane, was absent. The highest yields of **1** were realized by employing sodium or potassium cations for relatively short reaction periods (5-10 min) and by inversely neutralizing the reaction mixtures[5] (method A). For

SCHEME I



$$(C_6H_5)_2CH_2 + MNH_2 \overset{NH_3}{\rightleftarrows} (C_6H_5)_2CHM + NH_3$$

$$(C_6H_5)_2CHM \xrightarrow{C_6H_5N=NC_6H_5} (C_6H_5)_2CH\overset{M}{N}N(C_6H_5)C_6H_5 \;\; \mathbf{1'}$$

$$(C_6H_5)_2CHN(C_6H_5)NHC_6H_5 \;\; \mathbf{1} \xleftarrow{NH_4Cl} \mathbf{1'}$$

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[1] (a) Supported by the Petroleum Research Fund, administered by the American Chemical Society, on Grant 3710-A. (b) A preliminary report has been published; see E. M. Kaiser and G. J. Bartling, *Tetrahedron Lett.*, 4357 (1969). (c) Shell Fellow, 1971.

[2] (a) H. Gilman and J. C. Bailie, *J. Org. Chem.*, **2**, 84 (1937), and references cited therein; (b) G. A. Russell, R. Konaka, E. T. Strom, W. C. Danen, K.-Y. Chang, and G. Kaupp, *J. Amer. Chem. Soc.*, **90**, 4646 (1968), and references cited therein.

[3] P. F. Holt and B. P. Hughes, *J. Chem. Soc.*, 764 (1954).

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