Hydroxytropenylium Bromide.—Tropone (0.44 g, 4.15 mmol) was dissolved in absolute ethanol (10 ml) and 48% hydrobromic acid (1.18 g, 7.0 mmol) was added. Ether was added until turbidity persisted and the reaction was chilled at −10° overnight to afford a mass of white needles. The solvent was decanted and the crystals were washed with ether, dried *in vacuo*, and sublimed (80°, 1 torr) to yield 76.1% hydroxytropenylium bromide (0.59 g, 3.16 mmol) as pale yellow prisms. These crystals turn brilliant yellow at 125° and decompose above 170°.

Anal. Calcd for C_7H_7OBr: $C_7H_6OH^+$, 57.27; Br^-, 42.72. Found: $C_7H_6OH^+$, 56.9; Br^-, 42.91.

Hydroxytropenylium Bromide Monohydrate.—A freshly sublimed portion of hydroxytropenylium bromide was dissolved in oxygen-free water; this solution was allowed to evaporate to dryness in an oxygen-free glove box in which the vapor pressure of water was maintained at about 8 torr by a saturated solution of calcium chloride hexahydrate. This process affords hydroxytropenylium monohydrate as a mass of colorless, brittle spars and plates.

Anal. Calcd for $C_7H_9O_2Br$: $C_7H_6OH^+$, 52.20; Br^-, 38.95. Found: $C_7H_6OH^+$, 52.2; Br^-, 38.80.

Hydroxytropenylium Iodide.—Tropone (0.45 g, 4.25 mmol) was dissolved under nitrogen in deoxygenated absolute ethanol (10 ml) and 47% hydriodic acid (1.18 g, 4.4 mmol) was added. Anhydrous ether (80 ml) was added to precipitate a mixture of red and yellow crystals; these were washed with three 10-ml portions of ether, dried *in vacuo*, and sublimed (55°, 1 torr) to yield 86.0% hydroxytropenylium iodide (0.855 g, 3.66 mmol) as dark red prisms, mp 151–152° (lit.[13] mp 151°).

Hydroxytropenylium Iodide Monohydrate.—This material was prepared in the same manner as hydroxytropenylium bromide monohydrate, with the additional precaution that the preparation was carried out under red light. Evaporation of solvent water yielded hydroxytropenylium iodide monohydrate as orange spars which crush to a brilliant yellow powder.

Anal. Calcd for $C_7H_9O_2I$: $C_7H_6OH^+$, 42.50; I^-, 50.75. Found: $C_7H_6OH^+$, 42.4; I^-, 50.71.

Deuterioxytropenylium Bromide.—Boron bromide (1.06 g, 4.24 mmol) was placed in a small flask connected by a gas delivery tube to a second flask containing tropone (0.2 g, 1.9 mmol) in benzene (10 ml). Deuterium oxide (2 ml) was injected slowly into the boron bromide (*caution*) at a rate which maintained vigorous bubbling of deuterium bromide into the benzene solution. When the reaction was complete, the benzene was decanted from precipitated solids; these were washed with three 5-ml portions of benzene and dried *in vacuo* to yield deuterioxytropenylium bromide as a white microcrystalline powder. The infrared spectrum of this material was identical with that of hydroxytropenylium bromide with the exception of displacement of the O–H absorption.[3] This spectrum showed the sample to be contaminated with some hydroxytropenylium ion, even though the procedure had been carried out in a carefully dried glove box; this was shown to arise from residual water which is tenaciously retained by tropone, even on vacuum drying.[7,20]

Modified Preparation of Tropone. A. Ditropenyl Ether.[23-25]—Phosphorus pentachloride (108 g, 0.52 mol) was dissolved at reflux in carbon tetrachloride (800 ml) and a solution of cycloheptatriene (20 g, 0.22 mol) in carbon tetrachloride (400 ml) was added dropwise to this refluxing, vigorously stirred solution. The mixture was refluxed for 1 hr, then cooled, and allowed to stand overnight with protection from moisture; after this time, the flask was chilled in an efficient ice bath and distilled water (500 ml) added cautiously with stirring. The water layer was separated and retained; the carbon tetrachloride layer was discarded.

A 4-l., globe-shaped separatory funnel (Corning 6340) was clamped horizontally with the deep part in an ice bath on a magnetic stirrer; the neck of the funnel was fitted with a gas dispersion tube and a 60° funnel, both bent so as to reach the deepest part of the globe. A solution of 20% sodium hydroxide (500 g) was added and was deoxygenated by a stream of nitrogen; then the aqueous extract of tropenylium ion from the phosphorus pentachloride reaction was added slowly through the 60° funnel to the stirred, chilled base solution with continued bubbling of nitrogen. When addition was complete, the separatory funnel contained a snow-white emulsion of ditropenyl ether; this was extracted with three 200-ml portions of deoxygenated methylene chloride; magnesium sulfate was added to dry the methylene chloride extract; and this was again deoxygenated with a stream of nitrogen to remove air entrapped in the sulfate powder. The methylene chloride solution was brought to volume and an aliquot was extracted with 50% sulfuric acid; spectral analysis[16] of the acid extract showed the yield to be 77.8% ditropenyl ether (16.7 g, 0.084 mol) with a trace (less than 1%) of tropone.

B. Tropone and Cycloheptatriene.—The methylene chloride solution from the above preparation was placed over Linde 4A molecular sieve ($^1/_{16}$-in. pellets) and bubbled with nitrogen to remove air entrapped in the sieve. The flask was tightly stoppered, wrapped in foil, and stored in the refrigerator for 8 weeks. An aliquot was withdrawn and extracted with 50% sulfuric acid; spectral analysis[16] of this extract showed a yield of 97.5% tropone (8.69 g, 0.082 mol). Spectral analysis[16] of the methylene chloride remaining after acid extraction showed a yield of 97.2% cycloheptatriene (7.50 g, 0.0815 mol).

C. Hydroxytropenylium Ion Salts.—A portion of a methylene chloride solution prepared as above (100 ml) containing tropone (0.737 g, 6.9 mmol) and cycloheptatriene was concentrated to a volume of 20 ml, and hydrogen bromide passed over the surface of the stirred solution until precipitation ceased. Cyclohexane (50 ml) was added, the combined solvents were decanted, and the solid was washed with cyclohexane (50 ml) and dried *in vacuo* to yield 99.3% hydroxytropenylium bromide (1.28 g, 6.83 mmol) as a yellow powder.

Anal. Found: $C_7H_6OH^+$, 57.3.

A similar portion of the methylene chloride solution was concentrated at the rotary evaporator and the material not volatile at room temperature was taken up in deoxygenated absolute ethanol (15 ml) and 48% hydriodic acid (1.1 ml) was added. Dry ether (500 ml) was added and the mixed precipitate of red and yellow crystals was dried *in vacuo* to yield 67% hydroxytropenylium iodide (0.99 g, 4.2 mmol) as red crystals, mp 151°.

Registry No.—Hydroxytropenylium perchlorate, 16273-43-1; hydroxytropenylium chloride, 16273-44-2; hydroxytropenylium bromide, 16273-45-3; hydroxytropenylium iodide, 16273-46-4; ditropenyl ether, 16273-47-5; tropone, 539-80-0.

Acknowledgment.—We wish to thank Lee Louise Hesse, Catherine H. Burke, and Janice R. McMahon for technical assistance.

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[23] The preparation of tropenylium hexachlorophosphate is adapted from Kursanov,[24] and that of ditropenyl ether is adapted from Doering and Knox.[25] The specific procedures reported herein are designed to prevent losses from transfer operations, and discoloration and contamination from facile air oxidation.

[24] D. N. Kursanov and M. E. Vol'pin, *Dokl. Akad. Nauk SSSR*, **113**, 339 (1957).

[25] W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954).

Lithium Aluminum Hydride Reduction of Benzoyldiferrocenylphenylmethane[1]

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In connection with our synthesis work on the diketone (**1**) we were led to investigate the products of Clemmensen reductions of several ferrocenyl ketones (**2**) including benzoylferrocene (**2**, R = Ph). We established that products corresponding to **5** and **6** were formed along with the previously recognized products corresponding to **3** and **4**. Isolation of the former pair raised intriguing questions as to their mode of formation, and we have continued investigations into

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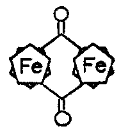
[1] Presented at the 19th Southeastern Regional Meeting of the American Chemical Society, Atlanta, Ga., Nov 1967, Abstracts, p 308.



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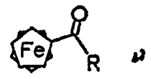

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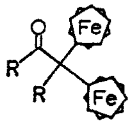

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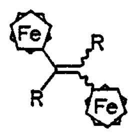

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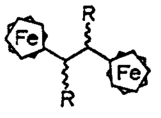

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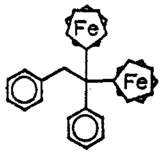

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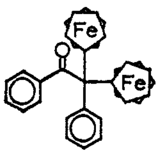

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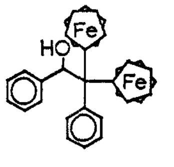

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these questions. In the meantime, the independent work of Rausch and Adams[2] has confirmed the presence of **5** and **6** (R = Ph) among the Clemmensen reduction products of benzoylferrocene with evidence similar to that gathered during that phase of our work.[3] The account by Rausch and Adams,[2] however, leaves unanswered an interesting point upon which we should like to comment.

Rausch, Vogel, and Rosenberg[4] first reported the isolation of a red-orange solid which decomposed when heated above 250°. Subsequently, Nesmeyanov and Kritskaya[5] suggested that this material was benzyldiferrocenylphenylmethane (**7**) formed by reduction of benzoyldiferrocenylphenylmethane (**8**) which they had also found among the products of Clemmensen reduction of benzoylferrocene. It is clear, however, from our own work, and now from the work of Rausch and Adams[2] as well, that the unknown material was **5** (R = Ph) and not **7**. Since Nesmeyanov and Kritskaya[5] had reported that the product of lithium aluminum hydride treatment of **8** in a separate experiment was identical with their Clemmensen reduction product (actually **5**), it was of interest to repeat the experiment in order to learn the source of the difficulty.

Lithium aluminum hydride reductions of ferrocenoyl compounds (**2**) in the presence of aluminum trihalide proceed to complete reduction, that is to say, formation of the corresponding ferrocenylmethyl compounds (**3**).[6] The same transformation also appears to be general for ordinary aryl ketones as well as for arylcarbinols;[7] the presence or absence of aluminum trihalide in the reported[5] reduction of **8** is problematical since the account of the work is devoid of experimental detail and previous claims of similar complete reductions[8] were later explained as probably due to the presence of aluminum trihalide.[9] We, however, elected to carry out the reduction in the presence of aluminum chloride.

Two products were found: the major one exhibited properties consistent with the expected alcohol (**9**), whereas the minor product was shown to be the olefin (**5**, R = Ph). Isolation of the red-orange olefin provided the basis of a reasonable explanation for the observation made by Nesmeyanov and Kritskaya,[5] for the red-orange solid of their Clemmensen reduction and their lithium aluminum hydride reduction was in fact the same, although it was not **7** as claimed by these authors but rather the recently established olefin (**5**, R = Ph).

The formation of **5** may easily be envisioned through formation of the benzylic carbonium ion from the benzilic alcohol (**9**). Ferrocenyl group migration in the former followed by deprotonation readily and reasonably accounts for the olefin. In the present work it is not clear whether the rearrangement took place during reaction work-up or during chromatography of the reaction product. In any case the point is of minor importance, for the absence of any experimental account for the original reduction[5] obviated an exact repetition of that experiment. The important point is that the isolation of the red-orange olefin in the present work suggests a rational explanation for what was clearly in contradistinction to the results obtained in this laboratory and to those obtained by Rausch and Adams[2] which established **5** (R = Ph) as the red-orange product of the Clemmensen reduction of benzoylferrocene.

Experimental Section

Reduction of Benzoyldiferrocenylphenylmethane (8) with Lithium Aluminum Hydride in the Presence of Aluminum Trichloride.—A sample of the pinacolone (**8**)[5] was carefully purified by two column chromatographies over alumina (Merck, acid washed). The compound was then shown to be pure to the limits of thin layer chromatography. Samples of 2, 5, 10, and 20 μg on silica gel were developed with 1:1 (v/v) benzene-hexane to show only one spot (**8**) with no trace of any spot corresponding to **5** (R = Ph).

A solution of the purified material (193 mg, 0.342 mmol) in 5 ml of anhydrous ether was added to a rapidly stirred slurry of lithium aluminum hydride (2.0 g, 53 mmol) in 25 ml of ether. This was then followed by addition of aluminum trichloride (3.5 g, 26 mmol) in 10 ml of ether. After the reaction mixture was stirred at room temperature during 4 hr, the excess hydride was carefully destroyed by dropwise addition of 2 ml of water and 4 ml of 20% aqueous sodium hydroxide solution. The material obtained from the ethereal phase and from several small ether extracts of the aqueous residue was combined and chromatographed on alumina. Only two bands developed during elution with the usual elutropic series of solvents. Benzene caused a small orange band to develop. The red-orange material obtained from this elution was shown to be **1,2-diferrocenyl-1,2-diphenylethene** (**5**, R = Ph) by direct comparison with authentic material where both were spotted together and in parallel on thin layer plates and developed with two different solvent systems, ether and 1:1 (v/v) benzene-hexane. This identity was confirmed by the identical electronic spectra determined from the two substances. Continued elution of the alumina column through the elutropic series of solvents did not produce any

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(2) M. D. Rausch and D. L. Adams, *J. Org. Chem.*, **32**, 4144 (1967).

(3) Structural assignments were aided materially by mass spectral studies carried out in collaboration with Henry M. Fales, National Heart Institute.

(4) M. D. Rausch, M. Vogel, and H. Rosenberg, *ibid.*, **22**, 903 (1957).

(5) A. N. Nesmeyanov and I. I. Kritskaya, *Izv. Akad. Nauk, SSSR, Otd. Khim. Nauk*, 352 (1962).

(6) See, for example, E. A. Hill and J. H. Richards, *J. Amer. Chem. Soc.*, **83**, 4216 (1961).

(7) For example see the work (as well as additional references) cited by B. R. Brown and A. M. S. White [*J. Chem. Soc.*, 3755 (1957)] and by R. F. Nystrom and R. A. Berger [*J. Amer. Chem. Soc.*, **80**, 2896 (1958)].

(8) A. N. Nesmeyanov, E. G. Perevalova, and Z. A. Bienoravichute, *Dokl. Akad. Nauk SSSR*, **112**, 439 (1959).

(9) M. Rosenblum, "Chemistry of the Iron Group Metallocenes: Ferrocene, Ruthenocene, Osmocene," John Wiley and Sons, Inc., New York, N. Y., 1965, p 147.

further development until methanol was used. In that solvent all of the remaining colored material was eluted, and the spectral data determined from the yellow solid (mp 78–80°) obtained on evaporation of the eluate were consistent with the alcohol, **2,2-diferrocenyl-1,2-diphenylethanol** (9): ir (CH_2Cl_2), 3590, 3510, 3420 (O–H), 3090, 3045, 3025 (aromatic C–H), 1600, 1575, 1500, 1450 (phenyl), 1100, 995 cm^{-1} (ferrocenyl); nmr ($CDCl_3$), δ 7.5–6.9 (complex multiplet, two, phenyl), 5.23 (s, one, CH–O or OH), 4.10 (s, ten, unsubstituted ferrocenyl rings), 4.18–3.70 (complex multiplet, nine, α and β ferrocenyl and CH–O or OH).

Registry No.—Lithium aluminum hydride, 1302-30-3; **8**, 12258-13-8; **9**, 12258-14-9.

Metal–Ammonia Reduction. II. Apparent Inhibition by Ferrous Metals[1]

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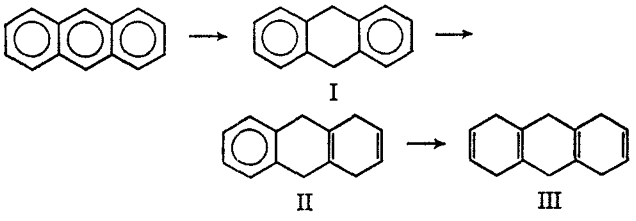
Received October 3, 1967

Conditions have recently been devised in this laboratory permitting the controlled, stepwise reduction of polycyclic aromatic hydrocarbons[2] by alkali metals dissolved in liquid ammonia.[3,4] A preliminary report[5] described procedures for the efficient conversion of 9,10-dihydroanthracene (I) into either 1,4,9,10-tetrahydroanthracene or 1,4,5,8,9,10-hexahydroanthracene (III), and also reported inhibition of this reduction by impurities in commercial ammonia or by iron salts. The essential features of the method are utilization of low lithium/hydrocarbon ratios and addition of the necessary proton source (*i.e.*, alcohol) late in the reaction period.



The inhibitory effects of trace metals and their salts which have been noted in scattered reports throughout the literature[4,6,7] have been the subject of speculation. However, aside from a study of the effect of colloidal iron on the Birch reduction of estradiol methyl ether,[8] the nature of the phenomenon has not been investigated. Dryden, Webber, Burtner, and Cella[8] conclude that iron interferes mainly by catalysis of the reaction between alcohol and alkali metal. Although this mechanism is probably valid when normal Birch conditions are employed (*i.e.*, alcohol present initially, generally in excess), it appears less certain for reactions conducted under other conditions.

TABLE I

REDUCTION OF ANTHRACENE (A) BY LITHIUM in AMMONIA[a]

Expt no.	Lithium, equiv	Metal salt added (1 equiv)	Product Composition,[b] % A	I	II	III
1	2.5	...	0	90	10	0
2	5.0	...	0	15	68	17
3	10.0	...	0	0	32	68
4	2.5	$FeCl_3$	0	100	0	0
5	5.0	$FeCl_3$	0	100	0	0
6	10.0	$FeCl_3$	0	100	0	0
7	5.0	$CoCl_2$	0	100	0	0
8	5.0	Nickel acetyl acetonate	0	100	0	0
9	2.5	Commercial ammonia	0	100	0	0
10	5.0	Commercial ammonia	0	85	15	0
11	10.0	$FeCl_3$[c]	0	0	41	59
12	10.0	$FeCl_3$[d]	0	100	0	0
13	10.0	$FeCl_3$[e]	100	0	0	0

[a] Lithium wire was added to a solution of 900 mg of the hydrocarbon in 75 ml of dry THF and 150 ml of distilled ammonia, and the solution was maintained at reflux (−33°) for 2 hr, then quenched by rapid addition of alcohol. [b] Percentages were determined from the integrated peak values in the proton nmr spectra of the product.[5] [c] Ferric chloride was added 2 hr after lithium, and 5 min before alcohol. [d] Ferric chloride was added 2 hr after lithium, and 2 hr before alcohol. [e] Anthracene was added 2 hr after other components, and 2 hr before alcohol.

A series of experiments with anthracene carried out under our standard conditions[5] (Table I) provides new insight into inhibition by metallic salts. In the absence of added salts, I–III are the sole products, and their ratio is highly dependent upon the number of equivalents of lithium present (expt 1–3). Ferric chloride, cobaltous chloride, nickel acetylacetonate, or impurities in ammonia powerfully inhibit reduction beyond the dihydro stage (expt 4–9), and relatively large excesses of lithium are insufficient to counteract this effect. In contrast, transformation of anthracene itself to I remains entirely unaffected. This apparent relative rapidity of anthracene 9,10-dianion formation is supported by additional experiments. Thus, rapidly quenched reactions (1–2 min) analogous to expt 3 and 6 exhibited essentially the same product distribution as the former experiment. That ammonia ($pK_a \sim 34$)[4] is ineffective as a protonating agent compared to alcohol ($pK_a = 16–18$) may be deduced from the failure of conversion of I into II or III, despite a 2-hr delay before addition of ferric chloride (expt 3 *vs.* 12).

Salts of ferrous metals are readily reduced to the metallic state by alkali metals in liquid ammonia,[9] and the free metals are catalysts for reaction of lithium with both ammonia[9,10] (eq 1) and alcohol[7] (eq 2).

$$e^- + NH_3 \longrightarrow NH_2^- + {}^1/_2H_2 \qquad (1)$$

$$e^- + ROH \longrightarrow RO^- + {}^1/_2H_2 \qquad (2)$$

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[1] This investigation was supported in part by Public Health Service Research Grant CA-08674 from the National Cancer Institute.

[2] Stepwise reduction of benz[*a*]anthracene through the dodecahydro stage is reported in paper III: R. G. Harvey and K. Urberg, *J. Org. Chem.*, **33**, 2206 (1968). Efficient single-stage transformation of a large number of polycyclic aromatic compounds will be reported shortly.

[3] A. J. Birch, *Quart. Rev.* (London), **4**, 69 (1950).

[4] H. Smith, "Organic Reactions in Liquid Ammonia," John Wiley and Sons, Inc., New York, N. Y., 1963.

[5] R. G. Harvey, *J. Org. Chem.*, **32**, 238 (1967).

[6] A. J. Birch, *J. Chem. Soc.*, 430 (1944).

[7] W. Hückel, B. Graf, and D. Münkner, *Ann.*, **614**, 47 (1958).

[8] H. L. Dryden, Jr., G. M. Webber, R. R. Burtner, and J. A. Cella, *J. Org. Chem.*, **26**, 3237 (1961).

[9] K. W. Greenlee and A. L. Henne, *Inorg. Syn.*, **2**, 128 (1946), and references therein.

[10] W. L. Jolly, University of California Radiation Laboratory Report UCRL-16046, 1965; W. L. Jolly and C. J. Hallada in "Solvent Systems," T. C. Waddington, Ed., Academic Press Inc., New York, N. Y., 1965; E. J. Kirschke and W. L. Jolly, *Science*, **147**, 45 (1965).