July, 1974] BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 47(7), 1709—1711 (1974) 1709

The One-electron Reduction of Carbonium Ions. VI. The Trapping of the Cycloheptatrienyl Radical with 2-Methyl-2-nitrosopropane in the Course of the Zinc Reduction of the Tropylium Ion*

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(Received January 5, 1974)

The zinc reduction of the tropylium ion was carried out in the presence of 2-methyl-2-nitrosopropane (a radical scavenger) in H_2O–THF (7: 3 by volume) at room temperature. In the reaction mixture with a short reaction time (5 min), *t*-butyl tropyl nitroxide (II) (a radical-trapping product) was identified by the ESR analysis. α-Phenyl-*N*-*t*-butylnitrone (I), which was isolated from the reaction mixture during a prolonged reaction time (30 min), was proved to be derived from the nitroxide II through the hydrogen abstraction by *t*-butyl nitroxide, which was itself formed from 2-methyl-2-nitrosopropane *in situ* in the acidic reaction mixture in the presence of zinc powder. The hydrogenation (on Pd/C) of the product mixture for a short reaction time (1 min) gave *N*-*t*-butyl-*N*-cycloheptylhydroxylamine and bicycloheptyl. On the basis of these observations, it is concluded that the primary product of the zinc reduction of the tropylium ion must be the tropyl radical.

The formation of bitropyl by the zinc reduction of the tropylium ion was first found by Doering and Knox.[1] They suggested an initial "one-electron" reduction, resulting in the formation of the tropyl (cycloheptatrienyl) radical, and a subsequent radical coupling. Since this mechanism seems certainly to be the most probable one, we have been considering the same mechanism in our series of studies of the reduction of substituted tropylium ions.[2] However, there has been no clear and direct evidence for the intervention of the tropyl radical in the course of the bitropyl formation. Thus, in order to confirm the validity of this mechanism, we have applied the "spin-trapping" technique[3] using *t*-nitrosobutane (2-methyl-2-nitrosopropane) to the zinc reduction of the tropylium ion.

Results and Discussion

The tropylium ion was allowed to react with an excess of zinc powder in the presence of 8 molar equivalents of *t*-nitrosobutane in H_2O–THF (7: 3 by volume) at room temperature for 30 min. The reaction products were then separated by elution chromatography to give bitropyl, α-phenyl-*N*-*t*-butylnitrone (I), and a comparable amount of *N*-*t*-butylhydroxylamine. The product distributions for the shorter reaction times were also examined to give the results summarized in Table 1.

The yields of bitropyl are almost invariable (50± 5%), whereas those of the nitrone I and *N*-*t*-butylhydroxylamine definitely increase with a prolonged reaction time. On the other hand, an analysis of the aqueous layer by means of ultraviolet spectroscopy revealed that the tropylium ion was completely consumed within one minute.

These results seem to indicate that the zinc reduction, which initially gives a primary product (presumably the tropyl radical), is rapidly completed and that about a half of the primary product so formed is trapped by *t*-nitrosobutane to give a transient product (II), which subsequently rearranges to the nitrone I[4] (see Scheme 1).

Table 1. The product distribution for the zinc reduction of the tropylium ion in the presence of *t*-nitrosobutane[a]

Reaction time, min	Temp. °C	Yield, %		
		Bitropyl	Nitrone I	Hydroxylamine[b]
1	24.0	50.4	4.4	~0
2	31.0	54.3	8.6	~0
15	31.0	45.5	32.0	~10.7
30	31.0	47.1	42.6	~21.0

a) [Tropylium fluoroborate]=1.91×10^{-2} M; [Zn]=5.0 atom equivalent with respect to the tropylium ion; [*t*-BuNO]=0.153 M; Solvent=H_2O–THF (7: 3 by volume).
b) *N*-*t*-Butylhydroxylamine; the yield is calculated with reference to the tropylium ion. The real yield of this compound is supposed to be greater; see Ref. 15 in the Experimental.

The attempt to isolate this transient product was unsuccessful because of its instability and volatility. However, the reaction mixture with a short reaction time (5 min), after the usual work-up and vacuum distillation, gave a red oil which, after an immediate dissolution in benzene, exhibited an ESR spectrum composed of an equivalent triplet of the doublet; this radical was assigned to be *t*-butyl tropyl nitroxide (II) (a_N=14.6 G, a_H=2.2 G), the trapping product. The identical ESR spectrum was observed in the reaction of *t*-nitrosobutane with the tropyl radical, which was itself produced by the thermal dissociation of bitropyl[5] in *m*-xylene at 60 °C (see Experimental). Furthermore, when the product mixture with a short reaction time (1 min) was catalytically hydrogenated on palladium-carbon, *N*-*t*-butyl-*N*-cycloheptylhydroxylamine (III), which was supposedly derived from the trapping product (the nitroxide II), was isolated (9% yield), along with bicycloheptyl, which was produced by the hydrogenation of bitropyl. These results are illustrated in Scheme 1.

The control experiments to examine the course of the

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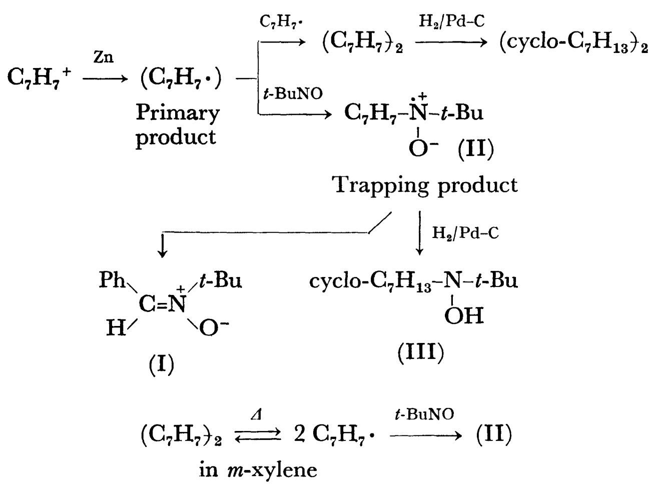
* Presented at the 24th Annual Meeting of the Chemical Society of Japan, Osaka, April, 1971.

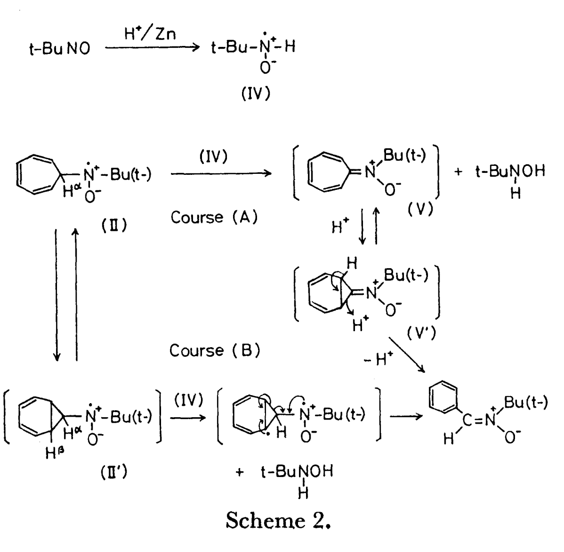


Scheme 1

formation of I indicated that the coexistence of three components, *i.e.*, *t*-nitrosobutane, zinc, and proton,[6] is a necessary condition in order to transform II into I. That is, the three reactions were continued for 30 min each after the immediate removal of the *t*-nitrosobutane (by bubbling off with air), zinc powder (by filtration), and proton[6] (by neutralization with NaOH) from the reaction mixtures with a short reaction time (1 min); no more than a trace amount of the nitrone I was detected in any of the reaction mixtures, whereas bitropyl was always found as the major product.

In another control experiment, the interaction of *t*-nitrosobutane with zinc in an aqueous tetrahydrofuran solution, acidified by the addition of acetic acid,[6] was found to give *t*-butyl nitroxide (IV), which was identified by means of its ESR spectrum (an equivalent triplet of doublet; $a_N=13.9$ G, $a_H=12.9$ G[7]). In addition, a nitroxide radical is known to be able to abstract a hydrogen atom.[8]

Consequently, it is most probable that, in the mixture with a prolonged reaction time, the nitroxide IV is produced *in situ* and that it immediately abstracts a hydrogen atom from the nitroxide II or its valence tautomer, II′, to give *N*-*t*-butylhydroxylamine. This is illustrated in Scheme 2.



Scheme 2.

In Course (A), the nitrone V would be produced by the abstraction of α-hydrogen of the nitroxide II, and would subsequently be converted into the nitrone I through a norcaradiene-type intermediate, V′, under acidic conditions in the reaction mixture or in the course of isolation, *e.g.*, during elution chromatography on silica gel.

As for Course (B), it is supposed that the cycloheptatriene-norcaradiene equilibrium lies to the norcaradiene side (II′) when the electron-withdrawing nature of the partially polarized N–O bond in the nitroxide II is taken into consideration.[9] The subsequent β-hydrogen abstraction from the norcaradienyl system (II′) to give the benzal system (I) seems plausible by analogy with the ionic rearrangements of a similar type found in the literature.[1,10] Thus, the preferred course (A or B) of the formation of the nitrone I from the nitroxide II has not yet been completely clarified.

However, on the basis of the ESR spectrum of the nitroxide II and of the isolation of the nitrone I and also the hydroxylamine III from the reaction mixture, it may be concluded that the primary product of the zinc reduction of the tropylium ion must be the tropyl radical.

Experimental[11]

Materials. Tropylium fluoroborate and *t*-nitrosobutane were prepared according to the methods of Conrow[12] and of Emmons[13] respectively. The zinc powder was of a reagent-grade quality. THF was distilled over 2,6-di-*t*-butyl-*p*-cresol; bp 66.0—66.2 °C.

Zinc Reduction of the Tropylium Ion in the Presence of t-*Nitrosobutane.* The Procedures for a representative run with the reaction time of 30 min will now be described. To a stirred solution of 0.750 g (4.20 mmol) of tropylium fluoroborate and 2.95 g (33.9 mmol) of *t*-nitrosobutane in 220 ml of H_2O–THF (7: 3 by volume), we added 1.38 g (21.0 mg-atom) of zinc powder under an atmosphere of nitrogen. After a 30 min reaction at 31 °C in the dark, the excessive zinc powder was filtered off. The filtrate was then worked up in the usual way to give 0.667 g of a partially-solidified red oil, which was then chromatographed over 25 g of silica gel (Nakarai, No. II-A, 100—200 mesh). Elution with *n*-hexane–benzene (4: 1 by volume) afforded 0.180 g (0.989 mmol) of bitropyl as white crystals, with an infrared spectrum identical with that of the authentic sample; 47.1% yield. The fractions eluted with benzene–ether (3: 2 by volume) gave 0.317 g (1.79 mmol) of the nitrone I as white crystals; its identity was established by means of the infrared and ultraviolet spectra and by a mixed mp; 42.6% yield; mp 73.0—74.5 °C (lit,[14] mp 75—76 °C). On the other hand, fractions eluted with ethanol and the ethereal extracts of the aqueous layer, which had been made alkaline, gave 0.0870 g[15] (0.978 mmol) of *N*-*t*-butylhydroxylamine as pale yellow crystals, which exhibited an infrared spectrum identical with that of the authentic sample; 2.9% yield based on *t*-nitrosobutane; 23.3% of the tropylium ion used.

In another run on half the scale of the above-mentioned reaction, after a reaction time of 5 min and the usual work-up, the reaction mixture was distilled under a vacuum to give 0.0184 g of a brownish-red oil; bp 70—85 °C (bath temperature)/0.4 mmHg. The distillate was immediately dissolved in benzene and sealed in a Pyrex tube (outer diameter, 4 mm) under a vacuum. An ESR spectrum was taken on the sample to give the results described in the text.

Hydrogenation of the Crude Product Mixture. In the same way as has been described above, 1.00 g (5.60 mmol) of tropylium fluoroborate was reduced with 1.83 g (28.0 mg-atom) of zinc powder in the presence of 3.90 g (44.8 mmol) of *t*-nitrosobutane in 292 ml of H_2O–THF (7: 3 by volume) at room temperature. After 1 min, the reaction mixture was worked up and concentrated *in vacuo* to *ca.* 10 ml, which was subsequently hydrogenated over 0.8 g of palladium carbon (Nakarai, 5%) in dry THF to give 0.519 g of a yellowish oil. From this oil we isolated 0.315 g (1.62 mmol) of bicycloheptyl (58% yield; NMR, τ_{CCl_4} 7.9 (br, m, 2H, methine), 8.5 (br, s, 24H, methylene); $\nu_{max}^{CCl_4}$ 1450 (sh), 1460, 2870, 2940 cm^{-1}) and 0.088 g (0.51 mmol) of *N*-*t*-butyl-*N*-cycloheptylhydroxylamine (9.2% yield; NMR, τ_{CCl_4} 6.3 (br, s, 1H, methine), 7.1 (br, s, 1H, OH), 8.5 (br, s, 21H, methylene, methyl); $\nu_{max}^{CCl_4}$ 1025, 1120, 1215, 1350, 1380, 1450 (sh), 1460, 2870, 2930, 3420, 3630 cm^{-1}), by the use of preparative thin-layer chromatography over silica gel (Merck, Kieselgel PF_{254}), with benzene–ether (2: 1) as the eluent.

Found: C, 71.53; H, 12.30%. Calcd for $C_{11}H_{23}NO$: C, 71.30; H, 12.51%.

Reaction of t-*Nitrosobutane with Zinc in an Acidic Solution. ESR Measurements.* Into a Pyrex tube (outer diameter, 10 mm) with a capillary side tube (outer diameter, 1 mm) for ESR measurement, we charged 0.020 g (0.23 mmol) of *t*-nitrosobutane and 0.10 g (1.5 mg-atom) of zinc powder. The tube was then connected to a vacuum line, and 1.6 ml of a solution of acetic acid (0.04 M) in H_2O–THF (1: 1 by volume) was transferred into the tube with vacuum distillation. After sealing off the tube under a vacuum, the mixture was shaken at room temperature in the dark and an ESR spectrum of the supernatant solution was immediately recorded to give the results described in the text.

Thermal Dissociation of Bitropyl in the Presence of t-*Nitrosobutane. ESR Measurements.* Into a Pyrex tube (outer diameter, 5 mm) for ESR measurement, we charged 0.015 g (0.17 mmol) of *t*-nitrosubutane and 0.090 g (0.50 mmol) of bitropyl, which had been purified by sublimation (50 °C/1 mmHg). The tube was then connected to a vacuum line, and 0.5 ml of dry *m*-xylene was added by vacuum distillation. After being sealed off under a vacuum, the tube was shaken well in the dark and introduced into the ESR cavity, which had been kept at 60 °C with JEOL variable-temperature equipment, JES-UCT-2X. After 10 min, signals composed of an equivalent triplet of a doublet (a_N= 14.5 G, a_H=2.2 G) began to appear in the ESR spectrum and kept increasing in intensity.

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2) a) K. Okamoto, K. Komatsu, and H. Shingu, This Bulletin, **42**, 3249 (1969); b) K. Okamoto, K. Komatsu, O. Murai, and O. Sakaguchi, *Tetrahedron Lett.*, **1972**, 4989; c) K. Okamoto, K. Komatsu, S. Tsukada, and O. Murai, This Bullein, **46**, 1780 (1973); d) K. Okamoto, K. Komatsu, O. Murai, O. Sakaguchi, and Y. Matsui, *ibid.*, **46**, 1785 (1973).

3) *cf.* E. G. Janzen, *Accounts Chem. Res.*, **4**, 31 (1971).

4) A control experiment indicated that the tropylium ion itself reacts slowly with *t*-nitrosubutane to yield a small amount (1.6%) of the nitrone I after 30 min at room temperature. However, 68.5% of the tropylium ion was recovered unchanged in this case. An ionic mechanism may be supposed to be operating.

5) Bitropyl is reported to yield the tropyl radical by homolytic thermal dissociation (G. Vincow, H. J. Dauben, Jr., F. R. Hunter, and W. V. Volland, *J. Amer. Chem. Soc.*, **91**, 2823 (1969)). Thus, it is most probable that the tropyl radical is trapped by *t*-nitrosobutane to give *t*-butyl tropyl nitroxide (II).

6) The acidity of an aqueous solution of the tropylium ion is reported to be almost equal to that of an aqueous solution of acetic acid (W. von E. Doering and L. H. Knox, *J. Amer. Chem. Soc.*, **76**, 3203 (1954)).

7) The lit. ESR: a_N= 13.4 G, a_H= 12.5 G (in methanol), a_N= 13.8 G, a_H= 13.8 G (in water); the ratio of a_N to a_H is strongly dependent on the solvent polarity (Th. A. J. W. Wajer, A. Mackor, and Th. J. de Boer, *Tetrahedron*, **25**, 175 (1969)).

8) For examples of such a hydrogen abstraction by the nitroxide radical, see a) R. Dupeyre and A. Rassat, *J. Amer. Chem. Soc.*, **88**, 3180 (1966); b) M. Iwamura and N. Inamoto, This Bulletin, **40**, 703 (1967); c) K. Murayama and T. Yoshioka, *ibid.*, **42**, 2307 (1969).

9) R. Hoffmann, *Tetrahedron Lett.*, **1970**, 2907; and the references cited therein.

10) a) D. Bryce-Smith and W. A. Perkins, *J. Chem. Soc.*, **1962**, 5295; b) A. G. Anderson, Jr., and L. L. Repologle, *J. Org. Chem.*, **28**, 262 (1963); c) P. Beresford, A. Ledwith, and H. J. Woods, *J. Chem. Soc.*, *B*, **1970**, 257.

11) The melting point and boiling point are uncorrected. The infrared and ultraviolet spectra were recorded with Shimadzu spectrometers, model IR-27 and model UV-50M, respectively. The ESR spectra were taken on a JEOL X-band spectrometer, model JES-3BS-X, equipped with a 100 kHz field modulation unit. The NMR spectra were taken on a Hitachi model R-24 spectrometer.

12) K. Conrow, "Organic Syntheses," Vol. 43, p. 101 (1963).

13) W. D. Emmons, *J. Amer. Chem. Soc.*, **79**, 6552 (1957).

14) W. D. Emmons, *ibid.*, **79**, 5739 (1957).

15) The observed yield of *N*-*t*-butylhydroxylamine may be somewhat lower than the real value because of the experimental loss caused by the high volatility of this compound.