

Cation Radicals. XXXII. Reaction of *N*-Ethylcarbazole with Iodine-Silver Salts.
Nitration of *N*-Ethylcarbazole (1,2)

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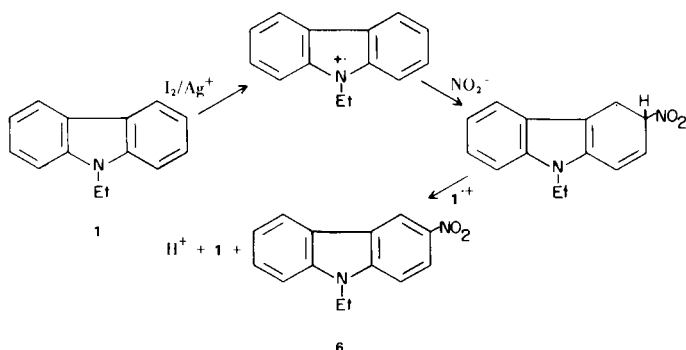
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Reaction of *N*-ethylcarbazole (**1**) with iodine-silver perchlorate gave a green solution having a singlet esr signal. Reduction of the solution with potassium iodide gave *N,N'*-diethyl-3,3'-dicarbazolyl (**3**, 48%). Small amounts of 3-iodo- (**4**) and 3,6-diiodo-*N*-ethylcarbazole (**5**) were also obtained. Compounds **4** and **5** are believed to have been formed by electrophilic iodination of **1** by I_2 -AgClO₄, whereas **3** appears to have been formed *via* the dimerization of $1^{+\cdot}$. In accord with this, reaction of **1** with iodine-silver nitrite gave 3-nitro-*N*-ethylcarbazole (**6**, 61%), 9% of another nitro-*N*-ethylcarbazole (**7**), thought to be either 1- or 4-nitro-*N*-ethylcarbazole, and 28% of **4**. Thus, trapping of $1^{+\cdot}$ by nucleophilic nitrite ion occurred even though $1^{+\cdot}$ is not stable enough toward isolation as the perchlorate.

Cation radicals have been implicated in several ways as intermediates in oxidative reactions of *N*-substituted carbazoles. Anodic oxidation of *N*-phenyl-, *N*-ethyl-, and several other *N*-alkylcarbazoles was found to be irreversible and to give the 3,3'-dicarbazyls *via* dimerization of the cation radicals (**4**). The cyclodimerization of *N*-vinylcarbazole (**2**) in oxidation by metal ions and by photosensitized oxygen-oxidation involves the *N*-vinylcarbazole cation radical (**5**), and so also, it is believed, does the polymerization of **2** brought about by reaction with *tris-p*-bromophenylammonium hexachloroantimonate (**6**), and a variety of other electron acceptors (**7**). Nitration of *N*-ethyl, *N*-isopropyl, and *N*-phenyl-carbazole by reaction with tetranitromethane is also thought to involve the corresponding cation radicals in cage reactions with nitrogen dioxide (**8**). Apart from these and similar reports, the chemistry of the cation radicals of *N*-substituted carbazoles has not been explored. We have had some success in making isolable cation radical perchlorates of heterocyclic and aromatic molecules by oxidation with iodine and silver perchlorate (**9,10**). We turned this technique to the oxidation of *N*-ethylcarbazole (**1**) to find that $1^{+\cdot}$ perchlorate was not isolable, although products attributable to the formation and reactions of $1^{+\cdot}$ were obtained. Thus, reaction of **1** with iodine-silver perchlorate in acetonitrile gave a green solution having a singlet esr signal. Reduction of the green solution with an excess of iodide ion gave, on work up, *N,N'*-diethyl-3,3'-dicarbazolyl (**3**, 48%). This, we believe, came from the reduction of $3^{+\cdot}$, which was the source of the green color and esr signal, and which had its origin in

the dimerization of $1^{+\cdot}$ and subsequent oxidation of the dimer (**11**). Also obtained were 3-iodo- (**4**) and 3,6-diiodo-*N*-ethylcarbazole (**5**) in poor yields, although insofar as **4** is concerned its poor yield was caused mainly by the difficulty in separating it from unused **1**. Iodine-silver perchlorate is an iodinating as well as an oxidizing agent (**12-14**) so that the formation of **4** and **5** is, in retrospect, not surprising. We do not attribute formation of **4** and **5** to reaction of iodide ion with $1^{+\cdot}$, since in all of our experience iodide ion reduces aromatic and heterocyclic cation radicals rather than adds nucleophilically to them.

Ristagno and Shine found that Perylene was easily mononitrated in reaction with iodine-silver nitrite, and recognized that attack of nitrite ion on the cation radical was involved (**10**). Application of this reaction to **1** led to 3-nitro-*N*-ethylcarbazole (**6**) in 61% yield. A second nitro-*N*-ethylcarbazole (**7**), m.p. 66-68°, was also formed in 9% yield, and is thought to be either 1- or 4-nitro-*N*-ethylcarbazole, neither of which appears to be recorded in the literature. Some of **4** was also obtained. The nitro derivatives of **1** (**6** and **7**) are thought to have been formed by reaction of $1^{+\cdot}$ with nitrite ion, most probably in a stepwise sequence as shown in Scheme 1. Thus, it appears that although $1^{+\cdot}$ was not isolable as the perchlorate, it is formed in the oxidations of **1** by I_2 -Ag⁺. When formed in the absence of a good nucleophile (*i.e.*, in oxidations by iodine-silver perchlorate) $1^{+\cdot}$ appears to be not sufficiently stable to resist dimerization. When formed in the presence of a nucleophile, *e.g.*, nitrite ion, trapping of $1^{+\cdot}$ appears to occur readily.



The use of iodine-silver nitrite with **1** is a very simple process for making **6**. Nitration of carbazoles by conventional means ordinarily gives mixtures of mono- and poly-nitrocarbazoles, although by controlled nitration with dilute nitric acid in acetic acid **6** can be prepared in 85% yield from **1** (15). In the use of iodine-silver nitrite the possibility of polynitration is avoided.

EXPERIMENTAL

N-Ethylcarbazole (**1**) was from Aldrich Chemical Company, and was recrystallized twice from ethanol. Acetonitrile was Eastman's anhydrous grade and was removed by syringe as needed from storage over molecular sieve in a septum-capped bottle.

Reaction of *N*-Ethylcarbazole (**1**) with Iodine-Silver Perchlorate.

To a stirred solution of **1** (490 mg., 2.5 mmoles) and silver perchlorate (514 mg., 2.5 mmoles) in 10 ml. of acetonitrile was added iodine (315 mg., 1.25 mmoles) under a nitrogen atmosphere. The reaction flask was protected from the light with aluminum foil. The mixture was stirred 3 hours, after which the green solution was reduced with excess of potassium iodide. After diluting with 200 ml. of chloroform, washing with sodium thiosulfate solution and water, and drying over magnesium sulfate, the solvent was removed at room temperature under reduced pressure. The solid residue was subjected to preparative-scale tlc, using silica gel (Merck GF-254) plates and pentane:chloroform (85:15 by vol) as developer. Each of four bands was redeveloped with benzene: pentane (1:4). The first band consisted of 234 mg. (48%) of *N,N'*-diethyl-3,3'-dicarbazolyl (**3**), m.p. 188.5-190° (lit. m.p. 193-194° (11)), mass spectrum parent peak at 388, nmr (deuteriochloroform): δ , 7.65 (m, aromatic, 14H), 4.20 (q, methylene, 4H), and 1.33 (s, methyl, 6H). The second band (150 mg.) consisted of a mixture of 3-iodo-*N*-ethylcarbazole (**4**), m.p. 83-84° (from petroleum ether), and **1**, which were separated in poor yields by fractional crystallization and identified by melting point and mixture melting point with authentic compounds. The third band consisted of 10 mg. (0.89%) of a solid with *m/e* 447 believed to be 3,5-diiodo-*N*-ethylcarbazole (**5**). The last band consisted of 19 mg. of an as yet unidentified

compound, m.p. 114-116°, parent peak mass 256.

The green color of the reaction solution is believed to have been caused by the presence of the cation radical of **3**. Prior to reduction with potassium iodide, the residue obtained gave a singlet esr signal.

Reaction of **1** with Iodine-Silver Nitrite.

The above procedure was used with 980 mg. (5 mmoles) of **1**, 770 mg. (5 mmoles) of silver nitrite, and 630 mg. (2.5 mmoles) of iodine in 30 ml. of acetonitrile. Tlc using pentane:benzene (4:1) gave 730 mg. (3.0 mmoles, 61%) of 3-nitro-*N*-ethylcarbazole, m.p. 126-127° (from heptane) (lit. (8) m.p. 126°), nmr (deuteriochloroform): δ , 8.10 (m, aromatic, 7H), 4.31 (q, methylene, 2H), and 1.40 (t, methyl, 3H). A second band gave a yellow solid, compound **7**, m.p. 66-68° (from pentane), *m/e* 240, nmr (deuteriochloroform): δ , 7.91 (m, aromatic, 7H), 4.42 (q, methylene, 2H), and 1.40 (t, methyl 3H).

Anal. Calcd. for C₁₄H₁₂N₂O₂: C, 69.99; H, 5.03; N, 11.65. Found: C, 70.20; H, 5.12; N, 11.41.

A third band gave 280 mg. (0.87 mmole, 28%) of **4**, m.p. 83-84° (from petroleum ether).

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