

A RADICAL REACTION OF TROPONE TOSYLHYDRAZONE
LEADING TO 2-TOSYLINDAZOLE

Katsuhiko Saito,* Takashi Toda, and Toshio Mukai
Department of Chemistry, Faculty of Science, Tohoku University,
Aoba, Aramaki, Sendai 980, Japan

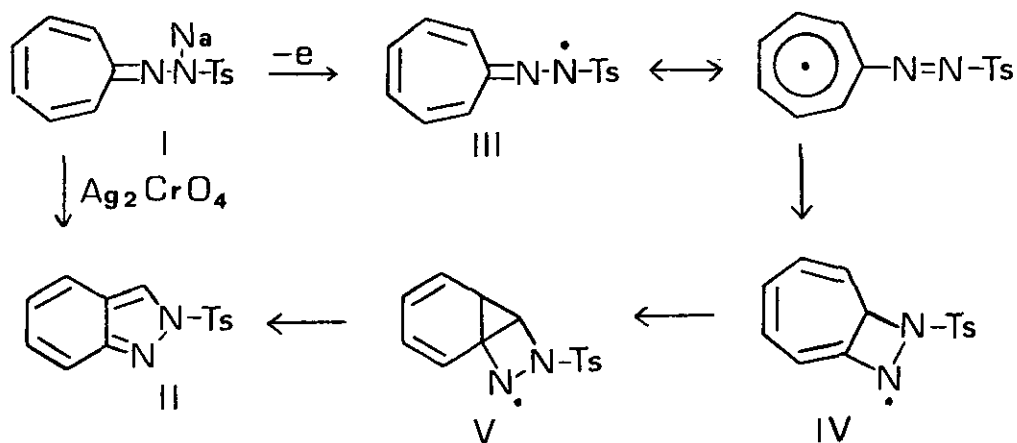
Silver chromate oxidation of tropone tosylhydrazone sodium salt (I) afforded 2-tosylindazole (II). The reaction is considered to proceed via an hydrazyl radical intermediate (III). Under the same reaction conditions m-nitrobenzaldehyde tosylhydrazone sodium salt provided m-nitrobenzotrile probably via m-nitrobenzylideneaminy radical.

Tropone tosylhydrazone sodium salt (I), on irradiation or heating, provided cycloheptatrienylidene, which added to electron-deficient olefins affording spiro[2.6]nonatriene derivatives.^{1,2} Furthermore, we found the formation of bitropyl, although in poor yield, from cycloheptatrienylidene via tropylium cation, when I was decomposed in the presence of some oxidative olefins.^{2b} In connection with this finding, we investigated the oxidation of I with silver chromate, in which case 2-tosylindazole (II) was

formed by an intramolecular cyclization of the corresponding hydrazyl radical (III). To achieve similar cyclization reactions, oxidation of m-nitrobenzaldehyde tosylhydrazone sodium salt was carried out, but only m-nitrobenzonitrile was isolated. Analogous oxidation was investigated with some other tosylhydrazone sodium salts, and however, the expected radical reactions did not take place. We wish to report an outline of these results.

When the sodium salt (I) was heated with 2 equiv of silver chromate in diglyme, 2-tosylindazole (II), mp 140°C, was obtained in 30 % yield. The silver chromate oxidation of tropone tosylhydrazone, instead of the sodium salt, also gave II in almost the same yield. The spectral properties of II are as follows: m/e, 272 (34 %, molecular ion peak), 208 (29 %), 155 (26 %), and 91 (base peak). IR (KBr): 3145, 3060, 1630, 1596, and 1380 cm^{-1} . UV (methanol); nm (log ϵ), 244 (4.40), 276 (3.60), 288 (3.73), and 296 (3.68). NMR (CDCl_3 , 100 MHz); δ 2.33 (singlet, 3H), 6.95-7.35 (multiplet, 4H), 7.5-7.7 (multiplet, 2H), 7.98 (doublet, 2H), and 8.60 (doublet 1H). These data suggest the structure of II to be 2-tosylindazole. The hydrolysis of II under basic conditions afforded indazole in 90 % yield. On the other hand, 1-tosylindazole,³ mp 112°C, which was synthesized from indazole by tosylation, was different from II, confirming the structure of II.

Upon consideration of the reaction mechanism from I to II, it reminds us that lead tetraacetate oxidation of tropone phenylhydrazone gave 2-phenylindazole via radical mechanism which was



reported by Tezuka, Yanagi, and Mukai.⁴ Thus, the reaction mechanism via the hydrazyl radical intermediate (III) might be proposed for the formation of II. The rearrangement of bicyclo[5.2.0] system (IV) to bicyclo[4.3.0] system (II) via norcaradiene form (V) is analogous to that of spiro[2.6]nonatriene system leading to indane system.⁵

In order to accomplish the cyclization of the hydrazyl radical giving indazole derivative, we attempted the silver chromate oxidation of sodium salt of m-nitrobenzaldehyde tosylhydrazone. However, no indazole was formed, and instead m-nitrobenzotrile was isolated in 7% yield. The result is similar to Binkley's finding that benzyldenaminyl radical leads to benzonitrile.⁶

Furthermore, the silver chromate oxidation was applied to the sodium salts of some styryl ketones and β -ionone tosylhydrazones, in which cases the corresponding pyrazole derivatives were obtained in fairly good yields. These reactions are considered to be

the reported base-induced pyrazole formation of α,β -unsaturated ketone tosylhydrazones.⁷

REFERENCES

- * Present Address: Department of Chemistry, Nagoya Institute of Technology, Gokiso-cho, Showa-ku, Nagoya 466.
- 1 (a) W.M. Jones and C.L. Ennis, J. Amer. Chem. Soc., 1967, 89, 3069; (b) W.M. Jones and C.L. Ennis, J. Amer. Chem. Soc., 1969, 91, 6391; (c) W.M. Jones, B.N. Hamon, R.C. Joins, and C.L. Ennis, Tetrahedron Letters, 1969, 3909; (d) L.W. Christensen, E.E. Waali, and W.M. Jones, J. Amer. Chem. Soc., 1972, 94, 2118; (e) W.M. Jones, Angew. Chem. Internat. Edit., 1972, 11, 325.
 - 2 (a) T. Mukai, T. Nakazawa, and K. Isobe, Tetrahedron Letters, 1968, 565; (b) K. Saito and T. Mukai, Tetrahedron Letters, 1970, 637; (c) K. Saito, Y. Yamashita, and T. Mukai, J.C.S. Chem. Commun., 1974, 58.
 - 3 K.v. Auwers, Ber., 1925, 58, 2081.
 - 4 T. Tezuka, A. Yanagi, and T. Mukai, Tetrahedron Letters, 1970, 637.
 - 5 K. Saito, T. Toda, and T. Mukai, Bull. Chem. Soc. Japan, 1974, 47, 331.
 - 6 R.W. Binkley, J. Org. Chem., 1970, 35, 2796.
 - 7 (a) G.L. Closs, L.E. Closs, and W.A. Boll, J. Amer. Chem. Soc., 1963, 85, 3796; (b) G. Ehe, Tetrahedron Letters, 1963, 1665.

Received, 28th March, 1975