FREE RADICAL TYPE ADDITION OF TOLUENESULFONYL CYANIDE TO UNSATURATED HYDROCARBONS

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Summary: By catalysis of AIBN, tosyl cyanide adds in a regio- and stereoselective manner to unsaturated hydrocarbons, including alkenes, dienes and l-hexyne. Accompanied intramolecular cyclization and ring cleavage were effected in reactions with norbornadiene, l,5-cyclooctadiene and pinenes.

Toluenesulfonyl cyanide (TsCN) has been successfully utilized in many synthetic aspects. Due to the strong induction of the sulfonyl group, TsCN functions as a CN transfer agent in reactions with C-, N-, O- and Snucleophiles.¹ The reaction is thought to involve an addition-elimination process. TsCN also undergoes cycloadditions readily with 1,3-dienes and 1,3dipolar species.² The reactivity is greatly enhanced by the effect of the sulfonyl group. The cycloaddition product from TsCN and cyclopentadiene is an especially useful intermediate in preparation of the carbocyclic analogs of nucleosides.³ However, the free radical type reaction of TsCN was rarely investigated except for a preliminary report of the photochemical reaction of TsCN with three alkenes, including an ambiguous stereochemical outcome in one example.⁴ We thus further exploited the free radical type addition of TsCN to a variety of unsaturated hydrocarbons.

Under an atmosphere of nitrogen, the reaction of TsCN (2.5 mmol) and an appropriate unsaturated hydrocarbon (25 mmol) was performed in refluxing benzene (or 1,2-dichlorobenzene, 25 mL) by initiation with AIBN (0.25 mmol). Exclusion of oxygen was necessary. The reaction was monitored by the TLC analysis, and the products were isolated by the chromatographic method. As shown in Table I, the reaction proceeded in a regio- and stereoselective fashion. A chain mechanism as depicted in the following scheme is proposed to account for this result.

$$\begin{array}{ccccccc} Me_2C(CN)N = NC(CN)Me_2 & \xrightarrow{\Delta} & 2 & Me_2C(CN) \\ Me_2C(CN) & + & TsCN & \longrightarrow & Ts & + & Me_2C(CN)_2 \\ Ts & + & & & \\ Ts & + & & & \\ C = C'_1 & \longrightarrow & Ts & - & \\ Ts & - & & & \\ Ts & - & & & \\ C = C'_1 & + & TsCN & \longrightarrow & Ts & - & \\ Ts & - & & & \\ C = C'_1 & + & TsCN & \longrightarrow & Ts & - & \\ \end{array}$$

Table I.

Entry	Substrate	Reac Temp. (°C)	tion Time (h)	Products ⁹	lsolated Yield, %
	~~~	80	18	$\begin{array}{c c} & & & \\ \hline & & & \\ (\underline{ig}) & & \\ CN & & \\ \hline & & \\ CN & & \\ CN & (\underline{ib}) \end{array}$	(jg): 76 (j <u>b</u> ): 10
2	$\bigcirc$	80	20	Ts CN (2)	70
3	A	80	6	X = Ts $Y (3a, b)$ $Ts$ $(3c) CN$	(3g) X=CN, Y=H: 72 (3b) X=H, Y=CN:6 (3c): 5
4	$\bigcirc$	120	16	H (4) NC	78
5	<<>>=	120	4	NC	71
6		120	36		15
7	$\bigcirc$	120	36	NC-5-TS (7)	16
8		60	24	NCTs ( <u>8</u> )	68
9	$\succ$	60	24	$\begin{array}{c} NC \longrightarrow Ts \\ (\underline{9}\underline{a}) \end{array} \xrightarrow{Ts} (\underline{9}\underline{b}) \end{array}$	(9g): 58 (9b): 30
10	~~=	80	36	NC H n-Bu H (10b)	( <u>IOg</u> ): 31 ( <u>IOb</u> ): 29

Entry 2 indicated this reaction occurred in the manner of anti addition. Similar stereochemistry was further revealed in reactions with norbornadiene and 1,5-cyclooctadiene to give <u>exo</u> adducts. Homoconjugative addition of TsCN to norbornadiene thus provided the major product (3a).⁵ With 1,5-cyclooctadiene, an intramolecular cyclization occurred to give the bicylic compound (4).⁶ On the other hand, addition of TsCN to  $\beta$ -pinene caused an opening of the strained four-membered ring to produce compound (5) in a 71 % yield.⁷ Similar reaction with  $\alpha$ -pinene afforded a low yield of product (6).

Although previous report has demonstrated that TsCN undergoes cycloaddition with 1,3-dienes,² we found 1,4-additions resulted in the free radical conditions. Thus, addition to cyclopentadiene gave a single product ( $\underline{8}$ ) in a modest yield. The reaction with 2,3-dimethyl-1,3-butadiene also produced the 1,4-adducts ( $\underline{9a}$ ) and ( $\underline{9b}$ ). On contrary to previous unsuccessful attempt,⁴ regioselective addition of TsCN to 1-hexyne was realized by catalysis of AIBN, but the reaction afforded two geometric isomers ( $\underline{10a}$ ) and ( $\underline{10b}$ ) in nearly equal amounts.

In summary, we provide an expedient method for preparation of compounds containing the cyano and sulfonyl groups. Since the chemistry of these functional groups are well developed, furthur application of our method in the organic synthesis is promising.⁸

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<u>Chem. Soc. 1964</u>, 86, 946. (c) Friedman, L. <u>J. Am. Chem. Soc</u>. 1964, 86, 1885. (d) Winkler, J. D.; Sridar, V. <u>J</u>. <u>Am</u>. <u>Chem</u>. <u>Soc</u>. <u>1986</u>, 108, 1708. (e) Haufe, G.; Alvernhe, G.; Laurent, A. <u>Tetrahedron Lett</u>. 1986, 27, 4449. 7. Oldroyd, D. M.; Fisher, G. S.; Goldblatt, L. A. J. Am. Chem. Soc. 1950, 72, 2407. 8. (a) Rappoport, Z. Ed. The Chemistry of the Cyano Group, 1970, Interscience Pub. (b) Jones, D. N. Ed. In <u>Comprehensive</u> <u>Organic</u> <u>Chemisry</u>, Pergamon: Oxford, 1979, Vol. 3, pp 171-213. 9. All products had satisfactory elemental analyses and compatible spectra (IR, MS,  1 H and  13 C NMR) for the proposed structures. Products (2), (3a),  $(\underline{3b})$ ,  $(\underline{4})$ ,  $(\underline{9a})$  and  $(\underline{9b})$  are colorless crystalline compounds.  $(\underline{2})$ , mp 136-138 ^oC (lit.  $4 133-135^{\circ}$ C); (3a), mp 212-214^oC (lit.  $10 211-212^{\circ}$ C); (3b), mp 109-110 ^oC (lit. ¹⁰ 107-110^oC); (<u>4</u>), mp 117-118^oC; (<u>9</u>a), 123-124^oC; (<u>9</u>b), mp 96-97^oC. The structures of (3a) and (4) were confirmed by X-ray diffractions (supplemental data are available on request). Some of pertinent ¹H NMR spectra (obtained in CDCl₂) are reported in  $\delta$  values: (<u>3a</u>), 1.68 (1 H, t, J = 5.1 Hz, H-6), 1.75-1.78 (2 H, m, H-1, H-2), 1.86 (1 H, d, J = 12 Hz, H-7), 2.39 (1 H, s, H-4), 2.44 (3 H, s), 2.51 (1 H, s, H-3), 2.55 (1 H, d, J = 12 Hz, H-7), 3.01 (1 H, s, H-5), 7.36-7.75 (4 H, m); (<u>4</u>), 1.24-1.34 (2 H, m), 1.85-2.07 (5 H, m), 2.18 (1 H, ddd, J = 15.4, 12.0, 5.5 Hz, H-3), 2.43 (3 H, s), 2.47 (1 H, m, H-1), 2.89 (1 H, ddd, J = 15.4, 12.5, 7.4 Hz, H-2), 2.98-3.04 (2 H, m, H-5, H-6), 7.34-7.74 (4 H, m); (5), 1.28 (3 H, s), 1.30 (3 H, s), 1.66 (1 H, m), 2.44 (3 H, s), 3.66 (2 H, s, H-7), 5.45 (1 H, br s, H-2), 7.36-7.75 (4 H, m); (8), 2.41 (1 H, ddd, J = 14.7, 4.5, 4.2 Hz, H-4 ), 2.43 (3 H, s), 2.82 (1 H, ddd, J = 14.7, 8.4, 2.7 Hz, H-4 ), 3.60 (1 H, ddd, J = 4.2, 2.7, 2.7 Hz, H-3), 4.32 (1 H, ddd, J = 6.4, 4.5, 2.1 Hz, H-5), 5.87 (1 H, dd, J = 5.6, 2.7 Hz, H-2), 6.04 (1 H, dd, J = 5.6, 2.1 Hz, H-1), 7.33-7.72(4 H, m); (<u>9</u>a), 1.40 (1 H, s), 1.84 (1 H, s), 2.42 (3 H, s), 3.03 (2 H, s), 3.82 (2 H, s), 7.33-7.70 (4 H, m); (9b), 1.73 (1 H, s), 1.85 (1 H, s), 2.44 (3 H, s), 3.03 (2 H, s), 3.80 (2 H, s), 7.33-7.76 (4 H, m); (10a), 2.45 (3 H, s), 2.79 (2 H, t), 6.82 (1 H, s), 7.36-7.76 (4 H, m). (10b), 2.41 (3 H, s), 2.63 (2 H, t), 6.23 (1 H, s), 7.32-7.76 (4 H, m). 10. Jagt, J. C. Ph. D. Thesis, Groningen University, The Netherlands, 1973, 78.

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