CHEMISTRY LETTERS, pp. 255-258, 1990.

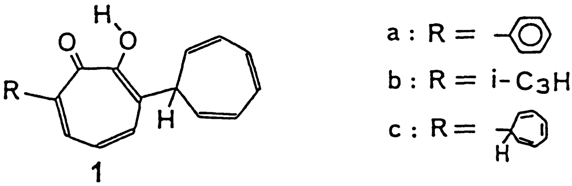
# Steric Compression-assisted Reaction in Tropolones.[1]
## Possible Generation of a Novel Resonance Hybrid in 3,7-Disubstituted Tropolones

Takahiro TEZUKA,* Hiroto KASUGA, Yoshinori ISAHAYA, and Tetsuo NOZOE†
Department of Chemistry, University of Tsukuba, Tsukuba 305
†Tokyo Research Laboratories, Kao Corporation, Bunka 2, Sumida-ku, Tokyo 131

The steric compression-assisted proton dissociation in 3,7-disubstituted tropolones generates a new resonance hybrid of the tropolone, which contains the tropylium ion moiety and proton. This resonance hybrid model explains the observed unusual chemical properties of 3,7-disubstituted tropolones.

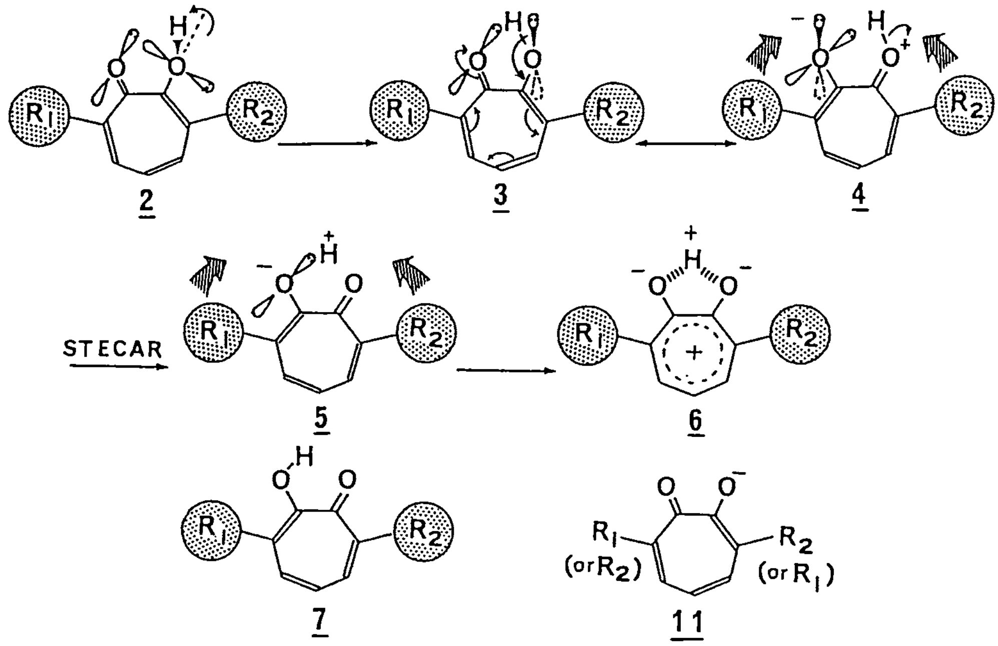
Recently, Tezuka et al. proposed a new concept of the steric compression-assisted reaction (STECAR) which proceeds in the following manner.[2-5] Steric repulsion by the bulky groups fixes first the conformation of the reacting moieties rigidly, and the steric compression effect thus substantiated induces polarization of these moieties, bringing about the specific reaction (see the scheme in Ref. 5).

In this paper, we report that the application of the same concept to 3,7-disubstituted tropolones (1a-c) deduces a new resonance hybrid model (6) that explains well the unusual chemical properties of 3,7-disubstituted tropolones (1a-c), which have remained as unsolved problems until now.[6-8]



1

We assume that steric repulsion by the bulky substituent ($R_2$) at the 3-position pushes both the hydroxy hydrogen and the lone pair electrons of the hydroxy oxygen in 2, rotating the OH group around the C-O bond axis to generate effectively 3 in which the hydroxy hydrogen is fixed in the perpendicular position to the tropolone $\pi$-orbital, and the hydrogen bonding with the lone pair electrons of the neighboring carbonyl oxygen at $C_1$ strengthens. In 3, on the other hand, the 2p-lone pair electrons of the hydroxy oxygen comes to the correct position to get good overlapping with the $\pi$-orbital of the tropolone ring.[9] This brings about a conjugated resonance form (4) in which the steric compression effect by $R_1$ and $R_2$ effectively causes dissociation of the proton to give 5 that generates a new resonance hybrid (6) as a consequence of the further steric compression-assisted reaction by the $R_1$ and $R_2$ groups. In 6, the proton stays intramolecularly between two oxygen atoms which take negative charges without leaving out of the molecule, and the tropolone seven-membered ring bears the tropylium ion property (Scheme 1). In the similar manner, 7 that is a valence isomer of 2 generates 6.



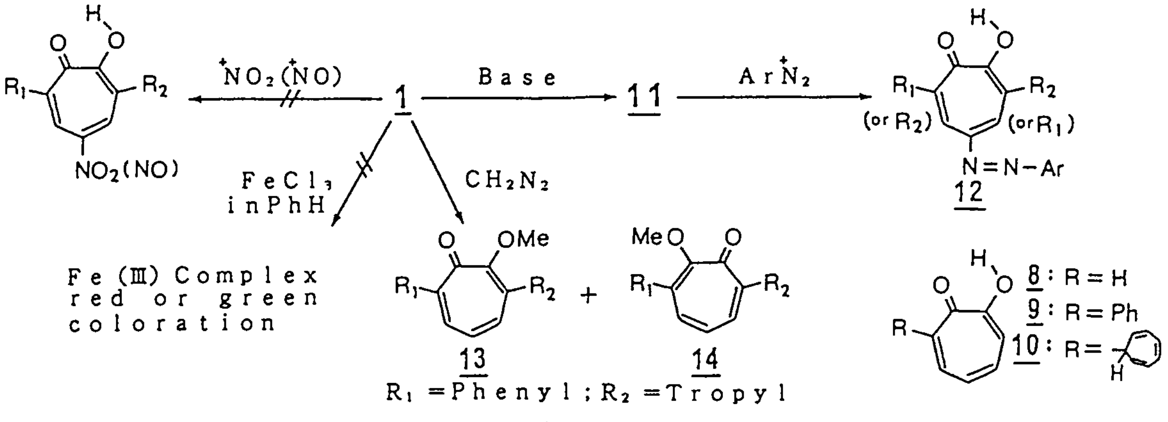
Scheme 1.

It is predictable that an increase in the bulkiness of the two substituent groups at the tropolone-$C_3$ and -$C_7$ increases the contribution of 6, and that the resonance hybrid (6) is stabilized in aprotic solvents. Abstraction of the proton from 6 by base gives rise to tropolonate anions (11).

The resonance hybrid formulism 6 is supported by the spectral data.[10-13] In the $^1$H NMR spectra in $CCl_4$ or $d_6$-benzene, the hydroxy hydrogen ($\delta$ 10 - 11 (broad signal)) and the tropolone ring protons of 1a-c (ca. $\delta$ 7.2 for 1a) appeared at lower fields as compared with those of the usual tropolones (8 - 10). The hydroxy hydrogen of 1a, for example, appeared at $\delta$ 10.92 as a very broad band peak with a band width of ca. 50 Hz in $d_6$-benzene at 100 MHz; the chemical shift is considerably low compared with that of tropolone (8) and 3-phenyltropolone (9) ($\delta$ 9 - 10 in $d_6$-benzene). Ditropyltropolone (1c) also showed a broad OH signal at the lower field ($\delta$ 10.76 in $CCl_4$) as compared with 3-tropyltropolone (10) ($\delta$ 10.24).[8] Both the $^{13}$C NMR shift of the tropolone ring carbon atoms of 1a ($\delta$ 171.8 - 135.7 in $CDCl_3$)[14] and the $^1$H NMR shift values (vide supra) indicate an appreciable cyclic conjugation in 6. It is worthy to note that the tropyl-$C_1$ and -$C_6$ hydrogens of 1c are shifted to the lower field ($\delta$ 5.36 in $CCl_4$) as compared with those of 10 ($\delta$ 5.24), suggesting that there is considerable proximity between the oxygen and tropyl groups in 1c to induce the steric compression-assisted reaction (STECAR) generating the resonance hybrid 6c.

In the IR spectra, 1a-c did not show the usual tropolone OH stretching absorption band at ca. 3200 $cm^{-1}$,[15] but they showed the OH band near the C-H absorption at 3050 $cm^{-1}$ region in KBr (disk) or $CCl_4$. In addition, the tropolone carbonyl bands of 1a-c (ca. 1600 and 1550 $cm^{-1}$) appeared with low intensity in KBr (disk), but they were obscure in $CCl_4$.

On the basis of the formulism 6, the observed unusual chemical properties of 1a-c are rationalized as follows (Scheme 2).6-8)



Scheme 2.

(1) The 5-position of the tropolone ring of 1a-c was found to be unsusceptible to the electrophilic attack by $^{+}NO_2$ and $^{+}NO$ in acetic acid, while tropolone is readily attacked by these species to give 5-nitro and 5-nitroso tropolones, respectively.16) This is explained as being due to the fact that the electron density of the tropolone ring of 1 diminishes due to the contribution of 6. In other words, the proton is captured so strongly between two oxygen atoms in 6, that the negative charge of the tropolone oxygen does not penetrate favorably into the seven-membered ring.

(2) On the other hand, under a basic condition 1a-c were diazo coupled at the 5-position to give 5-arylazo-3,7-disubstituted tropolones (12). This is due to the fact that by the action of base, 6 is converted to tropolonate anions (11) which react with diazonium ions at the 5-position as the usual tropolonate anions do (Schemes 1 and 2). It is important to note that 1a and 1b were diazo coupled by the pyridine catalyzed reaction, but 1c which has the most bulky group did not; 1c gave the diazo coupling product (12) when a mineral base such as sodium hydroxide was used. This is explained as follows. The contribution of the resonance hybrid is very strong in 6c, and the proton is deeply seated between two oxygen atoms due to the large steric compression effect by two bulky groups. Therefore, the strong base is necessary to generate 11 from 6c by abstraction of the proton.

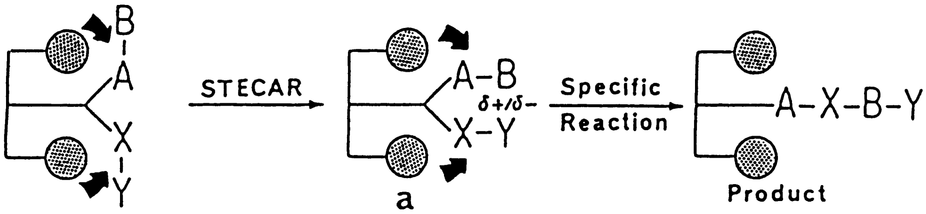
(3) The red and/or green coloration due to the chelate formation with Fe(III),16,17) which is most common with usual tropolones, did not take place with 1a-c in benzene. Only when alcohols were used as a solvent, the coloring due to the chelation with ferric chloride was observed. This can be explained on the basis of the resonance hybrid formulism 6. The chelating part (two oxygen atoms) is sterically hindered, and the proton is strongly captured by two anionic oxygen atoms in 6 in benzene.

(4) The reaction of 1a with diazomethane in diethyl ether gave two kinds of methyl ethers (13 and 14),7) supporting the resonance hybrid formulism 6.

The mechanism for the hydrogen shift in the tropolone, azophenine, and tetraphenylporphine systems has been discussed18-20) in relation to the proton tunneling. Form this point of view, the present results are interesting. In addition, the present study suggests applicability of the steric compression-assisted reaction concept (STECAR) to the various mechanistic problems.

References

1) Steric compression-assisted reaction (STECAR), part III. For part I and II, see Refs. 2 and 3.
2) T. Otsuka and T. Tezuka, Heterocycles, 26, 2081 (1987).
3) T. Tezuka and T. Otsuka, Chem. Lett., 1989, 1051.
4) T. Tezuka, T. Otsuka, H. Kasuga, and Y. Isahaya, Abst. 8th ISNA (Osaka), p. 169 (1989); T. Tezuka, H. Kasuga, T. Otsuka, and Y. Isahaya, Abst. 39th Symp. on Organic Reactions (Matsuyama), pp. 231 - 234 (1989).
5) The STECAR concept is visualized by the following scheme:



The most crucial point is fixation and polarization of the reacting moieties A, B, X, and Y as indicated by a. From this point of view, the concept of STECAR differs from that of the buttressing effect and B-strain.
6) T. Tezuka, Degree Thesis of D. Sc., Tohoku Univ. (1962); Bull. Chem. Soc. Jpn., 37, 1113 (1964).
7) T. Tezuka and T. Nozoe, Bull. Chem. Soc. Jpn., 52, 1867 (1979).
8) T. Nozoe, T. Tezuka, and T. Mukai, Bull. Chem. Soc. Jpn., 36, 1470 (1963).
9) O. Kikuchi, Tetrahedron Lett., 21, 1055 (1980).
10) We thank Professor Hiroshi Kakizawa for his suggestions on the NMR spectra.
11) H-O. Kalinowski, S. Berger, and S. Braun, "Carbon-13 NMR Spectroscopy," John Wiley & Sons (Chichester) 1984, pp. 301 and 307.
12) A Mori, S. Sugiyama, H. Mametsuka, K. Tomiyasu, and H. Takeshita, Buul. Chem. Soc. Jpn., 60, 4339 (1987).
13) H. Sugiyama, S. Ito, and T. Nozoe, Tetrahedron Lett., 1965, 179.
14) The $^{13}$C chemical shifts appearing at δ 171.8 and 167.2 can be assigned to the carbon atoms bearing the oxygen.
15) Y. Ikegami, "Kagaku No Ryoiki," Extra, Vol. 38, Nankodo (1959); R. L. Redington and T. E. Redington, J. Mol. Spectrosc., 78, 229 (1979).
16) T. Nozoe, K. Takase, H. Matsumura, T. Asao, K. Kikuchi, and S. Ito, "Dai Yuki Kagaku," Vol. 13, Asakura Pub. Co., Tokyo (1960).
17) Y. Oka and S. Matsuo, Bunseki Kagaku, 7, 215 (1958).
18) R. Rossetti and L. E. Brus, J. Chem. Phys., 73, 1546 (1980); Y. Tomioka, M. Ito, and N. Mikami, J. Phys. Chem., 87, 4401 (1983).
19) H. Sekiya, H. Takesue, Y. Nishimura, Z-H. Li, A. Mori, and H. Takashita, Chem. Lett., 1988, 1601.
20) H-H. Limbach, J. Hennig, D. Gerritzen, and H. Rumpel, J. Chem. Soc., Faraday Discuss., 74, 229 (1982); M. K. Holloway, C. H. Reynolds, and K. M. Merz, Jr., J. Am. Chem. Soc., 111, 3466 (1989).

(Received September 25, 1989)