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# ADDITION REACTION OF 4-METHYLENE-4H-HOMOCHROMENE DERIVATIVES WITH TETRACYANOETHYLENE. POSSIBLE INTERVENTION OF A BENZOHOMOPYRYLIUM ION INTERMEDIATE

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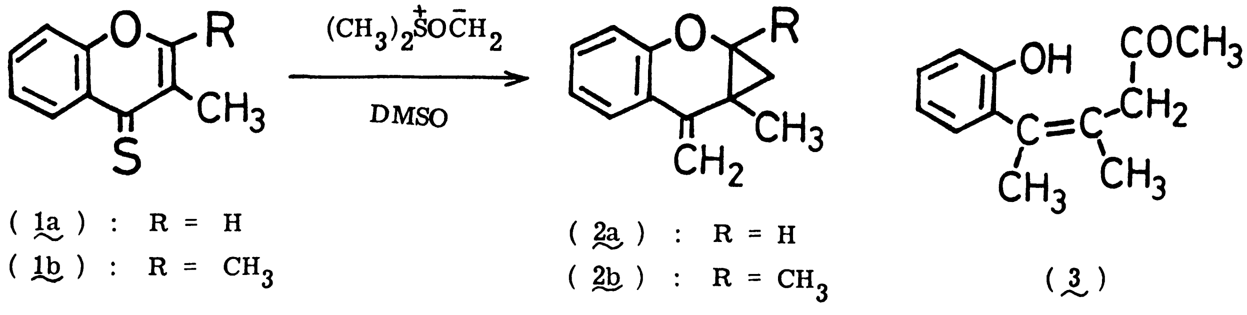
Vinylcyclopropane derivatives could be synthesized with one-pot procedure from α, β-unsaturated thione (chromothione) derivatives by dimethyloxosulfonium methylide. Extremely facile addition of tetracyanoethylene with 4-methylene-4H-homochromenes gave dihydrobenzoxazepine derivatives. The reaction may be well interpreted with the homoaromatic stabilization of the cationic part in a zwitterionic intermediate which would be formed at the rate-determining step.

The [2 + 2] cycloadditions of electron-rich olefins, e.g. p-methoxystyrene, vinyl ethers, and some vinylcyclopropanes, with tetracyanoethylene (TCNE) have been reported and explained to proceed through zwitterionic intermediates.[1] In a reaction of TCNE to 1, 1-diphenyl-2-vinylcyclopropane in 1, 2-dichloroethane at room temperature for 2 months, there was obtained unexpected product via zwitterionic intermediate by Shimizu, Nishida et al.[2] Now, the authors wish to report extremely facile formation of a similar sort of products in the reaction of TCNE with 3, 4-benzo-5-methylene-2-oxabicyclo[4. 1. 0]hept-3-ene (4-methylene-4H-homochromene) derivatives.

The substrates used in this investigation were prepared by the following method. Chromones were converted by $P_2S_5$[3] into corresponding chromothiones (1a) [mp 106-108°] and (1b) [mp 117-119°] , which were then treated with excess dimethyloxosulfonium methylide in dimethyl sulfoxide at room temperature for a few hours. After usual work-up processes the crude products were subjected to column chromatography on Silica Gel. Using light petroleum as the eluent both 2a and 2b were isolated as colorless oils[4] (10 and 30%, respectively), whose structures were speculated to 4-methylene-4H-homochromenes by the spectral data. Then, the structure of 2b was confirmed by comparing with the spectral characteristics and Rf-value on t. l. c. of the sample which was synthesized by Wittig reaction from 1, 6-dimethyl-3, 4-benzo-2-oxabicyclo[4. 1. 0]hept-3-en-5-one (homochromone). Homochromene (2b) was readily hydrolyzed quantitatively into a keto-phenol (3)[5] [mp 50-51° (from benzene-hexane)], which was also produced directly by the reaction of 1b with the ylide.

Although it has been reported that thiobenzophenone can be converted into 1,1-diphenylethylene via a thiirane with dimethyloxosulfonium methylide,[6] in the present case direct formation of vinylcyclopropane was accomplished from the α,β-unsaturated thione with the increment of two methylene groups.



(1a) : R = H
(1b) : R = $CH_3$

(2a) : R = H
(2b) : R = $CH_3$

(3)

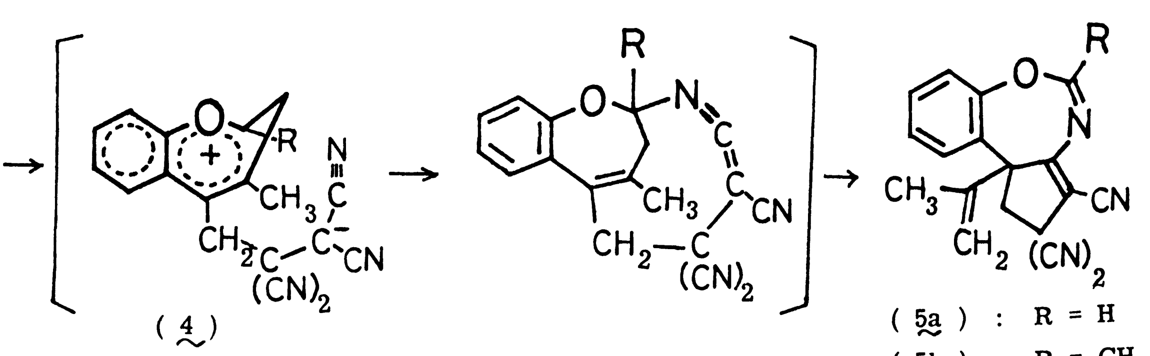
Scheme 1

When 2b was mixed with TCNE in various solvent such as chloroform, benzene, mesitylene, dioxane, 1,2-dichloroethane, and acetonitrile, colorless solids [mp 208-209° (from xylene)] were precipitated instantaneously even at room temperature in almost quantitative yield. The product was found to be one to one adduct of 2b and TCNE, whose structure was deduced as 5b[7] by the spectroscopic data and the hydrolysis to an enaminoacetate (6).[7] The reaction of 2a with TCNE analogously gave an adduct 5a[8] [mp 199-200° (from xylene)] under similar conditions.

Extremely facile formation of 5 may be explained by an initial rate-determining production of a zwitterionic intermediate, in which a cationic part should be highly stabilized by homoaromatic conjugation depicted in 4,[9] followed by ring closure at the nitrogen of the cyano group and then Cope rearrangement as shown in Scheme 2.

For the purpose of comparing with the above addition reaction, some standard vinylcyclopropanes (7a) and (7b) were treated with TCNE. Substrates for this investigation were prepared by the Wittig reaction of the corresponding cyclopropyl ketones. The ketone

(2)
+
TCNE



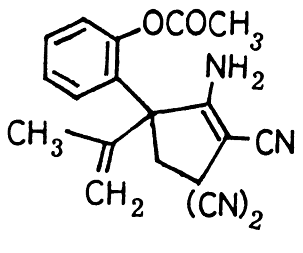
(4)

(5a) : R = H
(5b) : R = $CH_3$

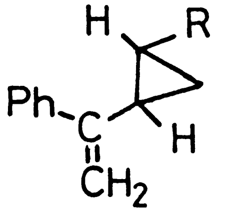
Scheme 2

7b was synthesized from phenyl vinyl ether with diazoacetophenone in benzene under reflux in the presence of Cu(acac)$_2$.

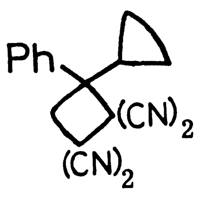
When 7a[10] [bp 92-93°/25mmHg] was mixed with TCNE in chloroform, colored solution resulted and then the color faded on standing a few days at room temperature. Evaporation of the solvent gave a colorless crystalline adduct [mp 153-154° (from carbon tetrachloride)] in 95% yield. On the basis of analytical and spectral data, this material was assigned to be a cyclobutane derivative (8)[11] holding a cyclopropane ring. The rate of cycloaddition of 7a was obviously increased in more polar solvent such as acetonitrile.[12] In contrast to the above results, 7b[13] [mp 36-37° (from light petroleum)] was recovered intact from the reaction mixture even though the reactants were heated under reflux in either chloroform or acetonitrile for a few days.



( 6 )



( 7a ) : R = H
( 7b ) : R = OPh

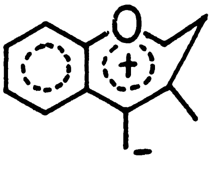


( 8 )

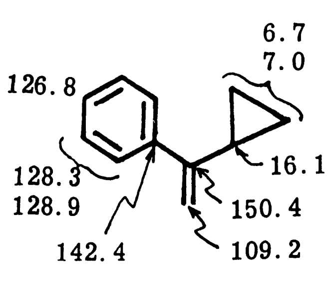
Judging from the high reactivity of 2 toward TCNE, significant contribution of the dipolar structure 9 may be anticipated in the ground state, however, there was found no appreciable difference among $\Delta\delta$ value (the difference of the $^{13}$CMR chemical shifts between exo-methylene carbons in 1,1-disubstituted olefins) for 2a, 7a, and 10[16] in contrast to the large $\Delta\delta$ value (98.6ppm) in the case of 7-methylenebicyclo[2.2.1]hept-2,5-diene.[14]

Accordingly, the extraordinary rate effect of 2a or 2b may be well interpreted in terms of higher polarizability of π-electrons in the exo-methylene group presumably caused by homoaromatic stabilization at the cationic part in the transition state (see Scheme 2). Kinetic studies on these addition reactions are now in progress.

The $^{13}$CMR Chemical Shifts in 1,1-Disubstituted Olefins

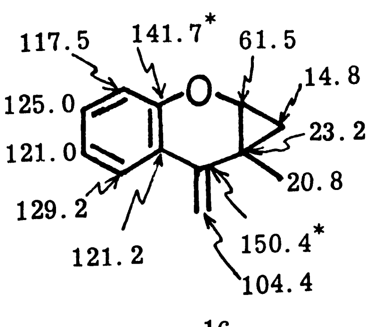


( 9 )



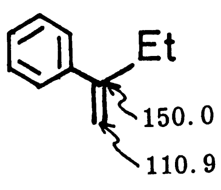
( 7a )[16]

$\Delta\delta$ = 41.2ppm



( 2a )[16]

$\Delta\delta$ = 46.0 ppm



( 10 )[15] $\Delta\delta$ = 39.1 ppm

* These assignments may be reversed each other.

## References and Notes

1. P. D. Bartlett, Quart. Rev., 24, 473 (1970); R. Huisgen, Acc. Chem. Res., 10, 117 (1977); S. Nishida, I. Moritani, and T. Teraji, J. Org. Chem., 38, 1878 (1973).
2. N. Shimizu, S. Ishizuka, T. Tsuji, and S. Nishida, Chem. Lett., 751 (1975); idem, J. Am. Chem. Soc., 99, 5972 (1977).
3. W. Baker, J. B. Harborne, and W. D. Ollis, J. Chem. Soc., 1303 (1952).
4. These compounds were somewhat air sensitive. **2a**: MS (m/e), 172($M^+$), 128; $\nu_{max}^{neat}$, 1610, 1225, 755$cm^{-1}$; PMR (δ, ppm in $CDCl_3$), 7.54-6.68(4H, m), 5.42(1H, s), 3.92(1H, q), 1.28 (3H, s), 1.4-1.2(1H, q), 0.82(1H, t, J=6Hz). **2b**: m/e 186($M^+$), 128; Found: C, 83.56; H, 7.56%. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58%; $\nu_{max}^{neat}$, 1610, 865, 750$cm^{-1}$; δ ($CCl_4$), 7.45-6.60(4H, m), 5.30(1H, s), 4.92(1H, s), 1.67(3H, s), 1.3(4H), 0.57(1H, d, 6Hz).
5. **3**: m/e 204($M^+$); Found: C, 76.14; H, 8.12%. Calcd for $C_{13}H_{16}O_2$: C, 76.44; H, 7.89%; $\nu_{max}^{nujol}$, 3400, 1700$cm^{-1}$; δ ($CCl_4$), 7.32-6.75(4H, m), 5.8(OH), 3.07(2H, s), 2.07(3H, s), 1.98(3H, s), 1.82(3H, s).
6. E. J. Corey and M. Chaykovski, J. Am. Chem. Soc., 87, 1353 (1965).
7. **5b**: m/e 314($M^+$); Found: C, 72.35; H, 4.49; N, 17.63%. Calcd for $C_{19}H_{14}N_4O$: C, 72.60; H, 4.49; N, 17.82%; $\nu_{max}^{nujol}$, 2220, 1655, 1605, 1250, 750$cm^{-1}$; δ ($CDCl_3$), 7.67-7.00(4H, m), 5.10(1H, s), 4.60(1H, s), 3.70(1H, d, 15Hz), 2.86(1H, d, 15Hz), 2.37(3H, s, -O-CMe=N-), 1.70(3H, s). **6**: m/e 332($M^+$); $\nu_{max}^{nujol}$, 3450-3230, 2220, 1765, 1650, 1640$cm^{-1}$ (after $D_2O$ exchange 2540, 2400(appeared), 1650, 1640(disappeared)); δ ($CDCl_3$), 7.4-7.1(4H, m), 5.63 ($NH_2$), 5.26(1H, s), 4.78(1H, s), 3.26(2H, s), 2.25(3H, s, -OCOMe), 1.93(3H, s).
8. **5a**: m/e 300($M^+$); Found: C, 71.87; H, 4.02; N, 18.36%. Calcd for $C_{18}H_{12}N_4O$: C, 71.99; H, 4.03; N, 18.66%; $\nu_{max}^{nujol}$, 2220, 1640$cm^{-1}$; δ ($CDCl_3$), 7.6-6.8(5H, m, aromatic and -O-CH=N-), 5.12(1H, s), 4.55(1H, s), 3.65(1H, d, 14Hz), 2.95(1H, d, 14Hz), 1.62(3H, s).
9. Similar cationic intermediate has been proposed on the solvolysis of the secondary ester; H. Yamaoka, K. Ohkata, and T. Hanafusa, Bull.. Chem. Soc. Jpn., 49, 245 (1976).
10. Addition reaction of chlorosulfonyl isocyanate to **7a** gave a [2 + 2] cycloadduct maintaining the cyclopropane ring; D. J. Pasto and A. Chen, Tetrahedron Lett., 713 (1973).
11. **8**: m/e 272($M^+$), 144; Found: C, 74.91; H, 4.80; N, 20.53%. Calcd for $C_{17}H_{12}N_4$: C, 74.98; H, 4.44; N, 20.57%; δ ($CDCl_3$), 7.5-6.8(5H, m), 3.57(1H, d, 13Hz), 3.15(1H, d, 13Hz), 2.0-1.5(1H, m), 0.9-0.0(4H, m).
12. The same product **8** was also formed as the single isolable product in acetonitrile.
13. **7b**: m/e 236($M^+$); Found: C, 86.31; H, 6.83%. Calcd for $C_{17}H_{16}O$: C, 86.40; H, 6.83%; $\nu_{max}^{neat}$, 1605, 1240, 750$cm^{-1}$; δ ($CDCl_3$), 7.6-6.9(10H, m), 5.30(1H, s), 4.88(1H, s), 3.66(1H, m), 2.08(1H, m), 1.4-1.0(2H, m).
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16. The authors are indebted to Mr. Ikebe, Hitachi Ltd., for his measurement of $^{13}$CMR spectra.

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