CHEMISTRY LETTERS, pp. 969-972, 1978. Published by the Chemical Society of Japan

# STEREOCHEMISTRY OF PHOTOCYCLOADDITION PRODUCTS OF ACENAPHTHYLENE WITH ACRYLONITRILE AND METHYL ACRYLATE

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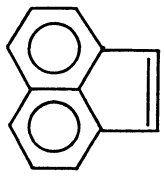
Stereochemistry of photocycloaddition products of acenaphthylene with acrylonitrile and methyl acrylate were decided by the chemical transformations and the NMR spectral correlation with those of their derivatives, viz., equilibriation of the deuterated isomers of acrylonitrile-adduct with t-BuOK/BuOD, reduction to amine with $LiAlH_4$, acetylation of amine, and hydrolysis followed by methylation of acrylonitrile-adduct to methyl acrylate adduct.

We have previously reported on the photocycloaddition of acenaphthylene(1) to acrylonitrile(2) and methyl acrylate(3) in micellar system.[1] Plummer and Hall have already proposed the stereochemistry of the adducts, syn isomer(mp. 80-82°) and anti isomer(mp. 139-141°),[2] those were given by the photoreaction of (1) with (2) in organic solvent. However, we now conclude that those compounds have to be reversed their stereochemistry by the following evidences from the chemical transformations and from the NMR data correlation with their derivatives.

Irradiation of acenaphthylene(1) with acrylonitrile(2) in 5% aq. PBC-34 gave two crossed-cycloaddition products, (4)[mp. 146-147°, 11.8%] and (5)[mp. 81-82°, 11.7%], in addition to the dimers of (1)[60.7%].[1] Both isomers, (4) and (5), exhibited nitrile band at around 2235$cm^{-1}$ in IR and the molecular ion($M^+$) at m/e 205 in MS. The NMR data are shown in the Table.

Treatment of (4)[30mg] with potassium t-butoxide[30mg] in t-BuOD[1ml] at 70-80° for 2h gave an equilibrium mixture of (4d)[mp. 147-148°, 11.1mg] and (5d)[mp. 81-82°, 11.8mg], separated by silicagel preparative thin layer chromatography with benzene. The similar treatment of (5)[30mg], also, gave a mixture of (4d)[11.6mg] and (5d)[

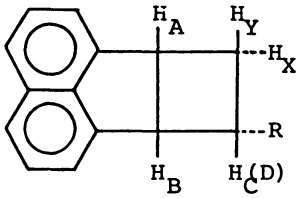


(1)

$CH_2$=CH-R

(2) R=-CN

(3) R=-$COOCH_3$



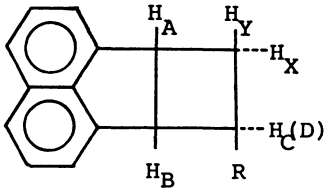
syn

(4) R=-CN

(6) R=-$CH_2NH_2$

(7) R=-$CH_2NHCOCH_3$

(10) R=-$COOCH_3$



anti

(5) R=-CN

(8) R=-$CH_2NH_2$

(9) R=-$CH_2NHCOCH_3$

(11) R=-$COOCH_3$

Fig. 1

12.4mg].[3] Both products exhibited quantitative deuterization of $H_C$ giving $M^+$ at m/e 206 in MS and showing disappearance of $H_C$ signal together with $H_C$-related couplings in NMR(see Table). The results show clearly that each proton of (4) and (5) at δ 3.85 and δ 3.00, respectively, should be of $H_C$. From our knowledge, the difference of $H_C$-chemical-shift between (4) and (5)[Δ:0.85ppm] should be based on the anisotropic effect of aromatic ring. Since (5) has higher chemical shift of $H_C$ at δ 3.00, it must be anti configuration, while (4) is syn as shown in Fig. 1.

The assignment was also supported by the following results. Treatment of (4) [20mg] with $LiAlH_4$[excess] in dry $Et_2O$ at 5-10° for 1h, then refluxing for 1h gave an amine(6) which was treated with $Ac_2O$-Pyridine to give N-acetyl compound(7)[mp. 130-132.5°, 92% from (4)]. Compound (5) under the same conditions, also, gave an amine(8) and acetate(9)[mp. 161-163°, 98% from (5)]. Both (7) and (9) exhibited amide bands at 3450 and 1667 $cm^{-1}$, and $M^+$ at m/e 251. $H_C$'s of anti, (8) and (9), at δ 2.17 and 2.18 appear in higher field than those of syn, (6) and (7), at δ 2.87 by the shielding effect of aromatic ring, while signals for nitrogen carrying methylene protons of (6) and (7), and N-acetyl methyl protons of (7) are in higher field than those of (8) and (9) by the same effect.

As shown in the Table, $H_X$'s of syn,[(4),(6) and (7)], are observed in higher field(Δ:0.22-0.75ppm) than those of anti,[(5),(8) and (9)]. These phenomena can well be understood when cyclobutane ring has the conformation shown as in Fig. 2. The conformation of cyclobutane ring might be twisted each other on opposite side by the substituent effect to put $H_X$ of syn over aromatic ring.

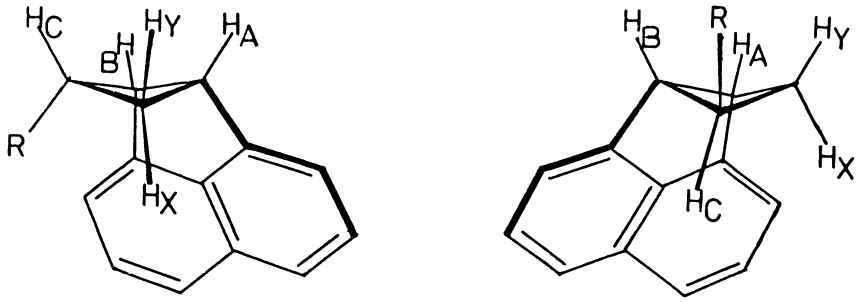
Irradiation of (1)[7.1mM] with methyl acrylate(3)[490mM] in 5% aq. PBC-34 gave two cycloaddition products, (10)[mp. 97-98°, 2.6%] and (11)[mp. 66-67°, 11.6%] in

Table The NMR spectral data of Adducts and Their Derivatives[a]

| Compound | $H_A$ and $H_B$ | $H_C$ | $H_X$ | $H_Y$ | $-CH_2N=$ | $CH_3$ |
|---|---|---|---|---|---|---|
| (4)[b] | 4.22 | 4.48 | 3.85 | 2.18 | 3.09 | |
| syn | dt | bt | ddd | dddd | dddd | |
| J's | ~9,6.5 | ~8 | 10,9,8.5 | 13,9,6.5,1 | 13,10,9,2 | |
| (4d) | 4.20 | 4.40 | — | 2.15 | 3.08 | |
| | m | m | | dd | dd | |
| | | | | 13,9 | 13,6.5 | |
| (5)[b] | 4.44 | | 3.00 | 2.40 | 3.00 | |
| anti | m | | m | m | m | |
| (5d) | 4.38 | | — | 2.35 | 3.06 | |
| | m | | | dd | ddd | |
| | | | | 13,4 | 13,8,2 | |
| (6) | 4.18 | | 2.87 | 1.43 | 2.87 | 2.16<br>2.30 |
| syn | m | | m | m | m | m |
| (7) | 4.20 | | 2.87 | 1.43 | 2.87 | 3.04 | 1.68 |
| syn | m | | m | m | m | m | s |
| (8) | 3.92 | | 2.17 | 2.17 | 2.17 | 2.93 | |
| anti | m | | m | m | m | m | |
| (9) | 3.90 | | 2.18 | 2.18 | 2.18 | 3.55 | 2.02 |
| anti | m | | m | m | m | m | s |
| (10) | 4.08 | 4.45 | 3.72 | 2.30 | 2.67 | | 3.33 |
| syn | m | m | m | m | m | | s |
| (11) | 4.23 | | 2.93 | 2.12 | 2.93 | | 3.72 |
| anti | m | | m | m | m | | s |

a The chemical shifts written by δ show a center of the signals. Aromatic ring protons are not presented in the table. Recorded in $CDCl_3$ with $Me_4Si$ as internal standard with a JMX-PMX 60 spectrometer. s; singlet, d; doublet, bt; broad triplet, m; multiplet J; coupling constant

b Recorded with JNM-FX 100




syn anti

Fig. 2 Twisted cyclobutane ring conformation

addition to the dimers of (1)[80%] after separation by $SiO_2$ p.t.l.c. Both isomers, (10) and (11), exhibited carbonyl band at 1722 and 1728 $cm^{-1}$, respectively, and $M^+$ at m/e 238. $H_C$ of anti(11) at δ 2.93 is shielded strongly than that of syn(10) at δ 3.72, while methyl protons of (10) at δ 3.33 is shielded highly than that of (11) at δ 3.72, both by the shielding effect of aromatic ring. The results show that compound (10) has to be syn, while (11) is anti. These assignments were also supported by the following chemical transformations.

Hydrolysis of anti(5)[70mg] with 20%aq.HCl-AcOH(1:1) under reflux for 3h, followed methylation with $CH_2N_2$, gave only (11)[98%], while those of syn(4)[84mg] gave (10) and (11)[83%, (10):(11)=97:3]. On the other hand, alkaline hydrolyses followed methylations of (4) and (5) did give always (11) by epimerizations.[4)]

According to our new stereochemical assignment of the cycloadducts, (4) as syn and (5) as anti, , experimental results of Plummer and Hall[2)] ( (5)/(4) carried the value of 3 to 4) can be clearly explained; viz., the stereoselective preference for anti over syn caused by a more efficient population of the triplet state in heavy atom containing solvent(heavy atom effect). We have also found the same phenomena, such as increasing the yield and the ratio of anti/syn in the case of photoreaction of (1) with (2) by the addition of 1-bromobutane in 5% aq. PBC-34.[1)]

References and Notes

1) Y. Nakamura, Y. Imakura, and Y. Morita, Chem. Lett., 965 (1978).

2) B. F. Plummer and R. A. Hall, J. Chem. Soc., Chem. Commun., 44 (1970).

3) Plummer and Hall[2)] have reported that syn-adduct(anti(5) as our new structure) was isomerized to only anti(syn(4) as our structure).

4) R. L. Petty, M. Ikeda, G. E. Samuelson, C. J. Briack, K. D. Onan, A. T. McPhail, and J. Meinwald, J. Am. Chem. Soc., 100, 2464 (1978).

(Received June 9, 1978)