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2, 3-디클로로-5, 6-디시아노-1, 4-벤조퀴논을 利用한 9, 10-디알킬-9, 10-디히드로안트라센 化合物의 수소이탈 반응

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Dehydrogenation of 9, 10-Dialkyl-9, 10-dihydroanthracene with 2, 3-Dichloro-5, 6-dicyano-1, 4-benzoquinone

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요 약. 2, 3-Dichoro-5, 6-dicyano-1, 4-benzoquinone을 이용하여 9, 10-dialkyl-9, 10-dihydroanthracene 계열 화학물의 수소이탈 반응이 진행되었다. Alkyl기의 크기가 클 수록 수소이탈 반응의 수득률이 적어지며 트란스화합물이 시스화합물 보다 반응이 빨리 진행됨이 확인되었다. 이들의 수소이탈 반응은 이온 메카니즘으로 설명되어진다.

ABSTRACT. A series of 9, 10-dialkyl-9, 10-dihydroanthracene has been dehydrogenated by 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone (DDQ) in good yields. The yield decreased with the larger alkyl groups in this 9, 10-dialkyl-9, 10-DHA series (DHA = dihydroanthracene). It is conceivable that *trans*-9, 10-diisopropyl-9, 10-DHA was dehydrogenated more rapidly than the *cis*-isomer, and, bassed on this observation, a concerted mechanism was ruled out and an ionic mechanism is proposed

INTRODUCTION

Dehydrogenation of polycyclic hydrocarbons has long been investigated intensively. Many methods including catalytic dehydrogenation over noble metals or reaction with reagents sulfur, selenium, chloranil, DDQ, and trityl salts have been adopted. Recently two new general methods were reported on the dehydrogenation of 9, 10-dialkyl-9, 10-DHA (DHA = dihydroanthracene) compounds. The first method involves the use of the *n*-butyllithium-*N*, *N*, *N'*, *N'*-tetramethylenediamine (TMEDA) reagent to generate dianionic intermediates which, on treatment with a suitable electron acceptor such as cadmium chloride, afford aromatic products.[1,2]

The second method employed a new reagent, trityl alcohol and trifluoroacetic acid, presumably involves trityltrifluoroacetate as the active species.[3] However, the former method is not applicable to compounds which do not readily form dianionic intermediates. Further more, when the substituted group in 9, 10-dialkyl-9, 10-DHA is isopropyl, dimers or isopropylidine derivatives are

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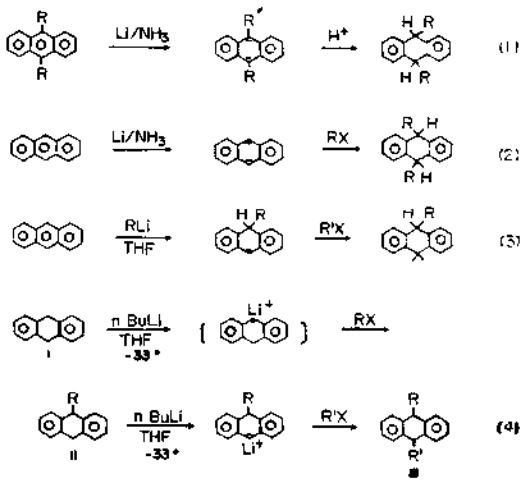
obtained. As to the latter method, 9, 10-dialkyl-9, 10-DHA compounds have not been studied throughly. In this respect we feel that DDQ 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone) should be explored to findout its availability. A comparison of the result of the dehydrogenation by DDQ to the *trans* and *cis*-isomers of those disubstituted DHA series could reveal the dehydrogenation mechanism of DDQ as well as the stereochemistry of the 9, 10-dialkyl-9, 10-DHA which has recently been studied mainly by nmr techniques.[4,5]

This report describes the use of DDQ in the dehydrogenation of representative ring systems, the effect of the alkyl substituents, the different reaction rate of the *trans* and *cis* isomers, the reaction mechanism and the nature of the intermediates, and the technique to distinguish the *trans* and *cis* isomers of 9, 10-dialkyl-9, 10-DHA.

RESULTS and DISCUSSION

There are converal convenient methods for the preparation of 9, 10-dialkyl-9, 10-DHA[2,4, 7~10] as depicted in equations (1)~(4), and the method (4) was employed in this study.



IIIa R=C_2H_5, R'=CH_3 IIId R=i-Pr, R'=C_2H_5
IIIb R=R'=C_2H_5 IIIe R=R'=i-Pr trans
IIIc R=i-Pr, R'=CH_3 IIIf R=R=i-Pr cis

The stereochemical assignment to each product in the above methods have intensively been discussed.[4,8] It was reported[11] that stereospecific *trans* isomers were obtained following the method (1), while stereospecific *cis* isomers were obtain in all the other methods. In the method (4) the *cis* isomer prevails over the *trans* one when the alkyl group is smaller. For the simplicity and for the purpose of our work *cis*-9-methyl-10-ethyl- and *cis*-9, 10-diethyl-9, 10-DHA (III*a* and III*b*) were selected. In the iso-

Table. 1 Deydrogenation of 9, 10-dialkyl-9, 10-DHA (III) by DDQ into 9, 10-dialkylanthracene (IV).

	R	R'		% Yield[a*,b*]	m. p (°C)	m. p in ref.
a	C_2H_5	CH_3	*cis*	48	143~145	145. 5[12]
b	C_2H_5	C_2H_5	*cis*	55	146~147. 5	147~147[13]
c	*i*-pr	CH_3	*trans*	72	97~99	98~99[2]
d	*i*-pr	C_2H_5	*trans*	70	110~110	110~110[2]
e	*i*-pr	*i*-pr	*trans*	41[c*] 65[d*] 72[e*]	168~170	169~170[7]
f	*i*-pr	*i*-pr	*cis*	20[c*] 31[d*] 38[e*]		

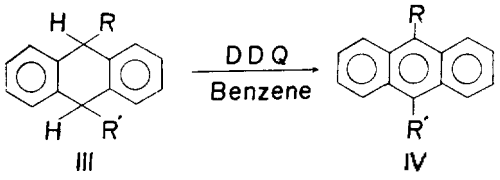
[a*] Yields are based on glpc and nmr data and represent product percentage composition rather than isolated yields of pure products.

[b*] Starting material was at all times existed in the final reaction mixture. Based on the nmr and glpc analyses, at least several side products accompanied in the reaction mixture.

[c*], [d*], and [e*] 12, 20 and 46 hr reaction time, respectively. Although reaction time longer than 20 hr could increase the yield, the isolated yield, however, is close to the one near 20 hr. It is due to the increase of side products in longer reaction time and much work is needed for purification.

propyl series all the *trans* isomer (IIIc~e) were selected, together with the *cis*-9, 10-diisopropyl-9, 10-DHA (III*f*).

Dehydrogenation of IIIa through III*f* by DDQ was carried out in dry benzene, and the results are given in *Table* 1. In each reaction a solution



III IV

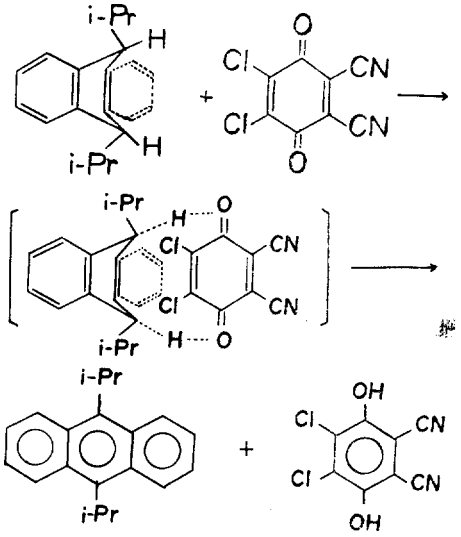
IVa R = C_2H_5, R'=CH_3 IVd R = i-Pr R'=C_2H_5

IVb R = R' = C_2H_5 IVe R=R'= i-Pr *trans*

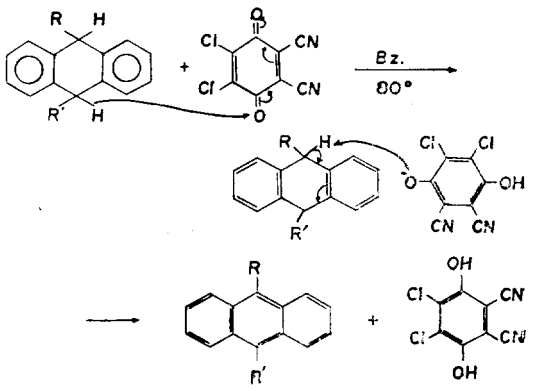
IVc R = i-Pr, R'=CH_3 IVf R=R'= i-Pr *cis*

of this DDQ in benzene is red because of the presence of a charge-transfer complex; as the dehydrogenation proceeds, the benzen-insoluble hydroquinone separates as pale yellow solid. During the reaction in reflux, a small amount of sample was removed and monitered. Since the prolonged reaction time could introduce unplesant side products, such as the hydroquinone (hydrogenated DDQ) forming adult product with the dialkyl-dihydroanthracene substrate, the reaction time chosen in this work should be the best for the highest yield. Moisture was also prevented from all the reaction, since trace of water can damage DDQ with the result of increasing side product.

As expected, the yield decreased with alkyl group becoming larger. This result is consistent with the hindrance consideration in the point that how easy the bulky DDQ approaches the substrate, plays the dehydrogenation role. It is interesting to point out that the rate of dehydrogenation of *trans*-9, 10-diisopropyl-DHA is faster than that of *cis* isomer. This result rules out a concerted mechanism (one-step mechanism), because a concerted mechanism requires to remove both protons of the subtrate on the same side as indicated below.

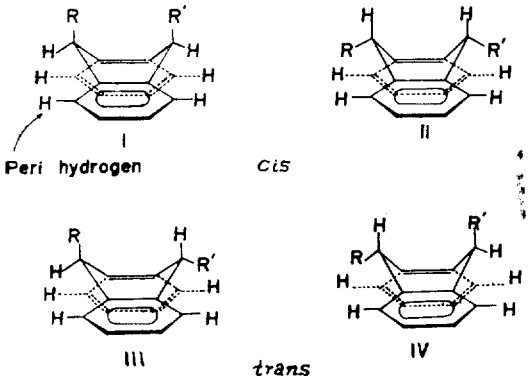


It has been attempted to investigate the possibilty of a freeradical mechanism. Therefore, following the same reaction condition reported, an initiator was added into each of the reactions. But neither dibenzoyl peroxide nor 2, 2'-azobis-2-methyl-propiontrile could increase the reaction rate of *cis*- and *trans*-9, 10-diisopropyl-DHA. Consequently a free radical mechanism is very unlikely. Our resulte agree with the literature report that the probable cause of this reaction involves the initial abstraction of a hydride ion, namely, an ionic mechanism.[14~16] This is illustrated in the following diagram:



It is believed that the dehydrogenation reactions of all the other dihydro compounds studied in this work by DDQ are proceeded by comparable mechanism.[14~16]

Our observation also provides a quick chemical method of distinguishing *cis*- and *trans*-9, 10-dialkyl-DHA. That is, the *trans* isomer is always dehydrogenated faster than that of the *cis* isomer. This could be explained by their stereoconfigurations. For the *cis* isomer both protons can be at pseudoequatorial (I) or at pseudoaxial (II) positions. Clearly, due to the steric hindrance between the alkyl groups and the peri hydrogen in the aromatic ring, configuration II is much more unstable than configuration I. Consequently, configuration I



is assumed to exist in the real compound. From this view it is clear that the proton in the pseudoequatorial position should be more difficult to be abstracted by DDQ. However, when the *trans* isomer is concerned, either configuration III or configuration IV provides one proton always at pseudoaxial position which is more accessible to be abstracted by DDQ. Based on this steric reason, it is conceivable that the *trans* isomer is dehydrogenated faster than that of the *cis* one, and therely that the dehydrogenation reactions studied in this work are proceeded by an ionic mechanism.

EXPERIMENTAL

Physical Measurement and Materials. All reactions were carried out under atmospheres of nitrogen using standard techniques. Benzene, ethyl ether, tetrahydrofuran (THF), cyclohexane and TMEDA were refluxed and distilled over lithium aluminum hydride. *n*-Butyllithium (2.4 *M* in hexane) was obtained from Alfa Inorganics, and was always introduced to the reaction vessel by syringe to insure free from moisture. Proton nmr spectra were obtained on Varian T-60 and A-60 MHz spectrometers, and chemical shifts are reported relative to tetramethylsilane (TMS) in $CDCl_3$ or CCl_4 and coupling constants in hertz. Integration was consistent with all assignments. Gas chromatographic analyses were performed on a Barber Coleman Flame Ionization Gaschromatograph model 5320 using a 6 ft $\times$ 1/8 in. column of 10 % SE-30 on Chromosorb W. Melting points are uncorrected.

Preperation of 9-Ethyl-9, 10-DHA and 9-Isopropyl-9, 10-DHA. These were prepared according to the method reported in the literature.[2,4] The yields are higher and the reactions are easier to control when alkylation of DHA are performed using *n*-butyllithium, other than the emplyment of mtetal ammonia alkylation.

Preparation of 9, 10-Dialkyl-9, 10-DHA. The *cis*-9-methyl-10-ethyl, -*cis*-9, 10-diethyl-, *trans*-9-methyl-10-isopropyl, -*trans*-9-ethyl, -10-isopropyl, -and *trans*-9, 10-diisopropyl-9, 10-DHA were obtained through the alkylation of 9-ethyl-9, 10-DHA or 9-isopropyl-9, 10-DHA with *n*-butyllithium and the appropriate alkyl bromide under the conditions similar to monoalkylation of DHA. In a typical reaction of *n*-butyllithium (12 mmole) in hexane was added to a stirred solution of 9-isopropyl-9, 10-DHA (2.5g, 11.2 mmole) in dry THF (100 m*l*) at $-33°$ under a nitrogen atmosphere. The resulting solution was

maintained at this temperature for 40 min, then cooled to the range −60 to −78° and stirred an additional 40 min. A stream of gaseous methyl bromide was then introduced rapidly (through a tube of Ascorite) into the solution over a 3 minute period and then the reaction quenched by addition of solid NH_4Cl (20 g). Addition of water and ethyl ether afforded an oil. Gas chromatography showed the presence of *trans*-9-methyl-10-isopropyl-9, 10-DHA, an unidentified compound, and the starting material. *Trans*-9-methyl-10-isopropyl-9, 10-DHA was obtained by means of column chromatography over alumina as white solid with the yield of 42 %. Recrystallization of this material gave it as white needles, m. p 76∼77° (lit.[4] 76∼77°): nmr spectrum is identical to the one reported.[4] The unidentified material, never being attempted to purify or identify, is assumed to be the *cis*-9-methyl-10-isopropyl-DHA. All the other *trans*-9, 10-dialkyl-9, 10-DHA were prepared in similar manner, and those physical properties, such as m. p and nmr data, have been examined and consistent with the reported results.

Preparation of *cis*-9, 10-Diisopropyl-9, 10-DHA. This compound was prepared as a side product during the preparation of *trans*-9, 10-diisopropyl-9, 10-DHA. Upon chromatography over basic alumina eluted with hexane, the *trans* isomer was eluted out first, and then followed by the *cis* isomer which was recrystallizedt wice from ethanol as white needles: m. p 108∼109° (lit.[6] 109∼110). An alternative method to prepare this compound is the metallation of anthracene in THF with excess methyllithium followed by addition of excess isopropyl iodide. However, this method was not adopted.

Dehydrogenation of 9, 10-Dialkyl-9, 10-DHA (IIIa∼f) by DDQ. In a typical experiment a solution of *trans*-9-methyl-10-isopropyl-9, 10-DHA (2 mmole), DDQ (2 mmole) and 30 *ml* of dry benzene was refluxed for 20 hr under the atmosphere of nitrogen. After cooling to room temperature, the reaction mixture was passed through a short silica column (2.5×8 cm) via elution with benzene to remove the by-product 2, 3-dichloro-5, 6-dicyano-1, 4-benzoquinone. Analyses of the eluent indicated that 9-methyl-10-isopropylanthracene was produced in 70 % yield. Chromatography on neutral alumina and elution with hexane, followed by crystallization from petroleum ether, provided pure 9-methyl-10-isopropyl anthracene: m. p 97∼99° (lit.[2] 98∼99): nmr (CCl_4) 1.75 (*d*. 6, J=7.5 Hz), 3.03 (*s*. 3), 4.55 (*m*. 1, J=7.5Hz), 7.22∼7.56 (*m*. 4), and 8.10-8.60 ppm (*m*. 4). Analogous reactions of the other 9, 10-dialkyl-9, 10-DHA compounds was preceded in a similar way to afford the related anthracences (IV *a*∼*b* and IV*d*,*f*) with the yields shown in *Table* 1. In the case of *trans*- and *cis*-9, 10-diisopropyl-9, 10-DHA (III*e* and III*f*), the yields at various refluxing time (other than those shown in *Table* 1) are as follows: 9 hr reflux: *trans*, 22 % and *cis*, 8 %; 15 hr reflux; *trans*, 57 % and *cis*, 22 %; 26 hr reflux: *trans*, 65 % and *cis*, 30 %. The structures of all the foregoing compounds were confirmed by nmr and glpc analyses in comparison with the authentic compounds.[7,8]

Dehydrogenation of *trans*-and *cis*-9, 10-Diisopropyl-9, 10-DHA by DDQ with Initiator. Similar experiments were conducted as shown above except that 20.0 mg of dibenzoyl peroxide was introduced in each reaction involving *trans*- or *cis*-9, 10-diisopropyl-9, 10-DHA. After, the reaction mixture was refluxed for 30 hr, glpc and nmr analyses indicated that the yields were not increased. The reaction rate did not increase either when 2.0 mg of 2, 2-azobis-2-methylpropiontrile was used in separate reactions.

Epimerization of *trans*-9, 10-Diisopropyl-9, 10-DHA into *cis*-9, 10-Diisopropyl-9, 10-DHA. To a solution of *trans*-9, 10-diisopropyl-9, 10-DHA (1mmole) in dry cyclohexane (10 m*l*) and

TMEDA (four-fold molar ratio) was added a solution of *n*-butyllithium (five-fold molar ratio) in hexane. The resulting deep red-purple solution was maintained at reflux for 1.5 hr, cooled (in 10 min), and the reaction mixture was discharged by addition of water. Conventional workup afforded essentially quantitative recovery of products shown by glpc and nmr to consist of only *cis*- and *trans*-9, 10-diisopropyl-9, 10-DHA in the ratio of 92 to 8.

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REFERENCES

1. R. G. Harvey and H. Cho, *J. Amer. Chem. Soc.*, **96**, 2434(1974).
2. R. G. Harvey, L. Nazareno, and H. Cho, *ibid.*, **95**, 2376(1975).
3. P. P. Fu and R. G. Harvey, *Tetrahedron Letters*, **36**, 3217(1974).
4. H. E. Zieger and L. T. Gelbaum, *J. Org. Chem.*, **37**(7), 1012(1972).
5. E. J. Panek and T. J. Rodgers, *J. Amer. Chem., Soc.*, **96**, 6921(1974).
6. H. E. Zieger, D. J. Schaeffer, and R. M. Padronaggio, *Tetrahedron Letters.*, 5027(1969).
7. R. G. Harvery, L. Arzadon, J. Grant, and K. Urberg, *J. Amer. Chem. Soc.*, **61**, 4535(1969).
8. R. G. Harvey and L. Arzadon, *Tetrahedron*, **25**, 4887(1969).
9. D. Nicholls and M. Szware, *J. Amer. Chem. Soc.*, **88**, 5757(1966).
10. D. Nicholls and M. Szware, *Proc. Roy. Soc. London, Azol*, 231(1967).
11. R. G. Harvey and C. C Davis, *J. Org. Chem.*, **34**, 3067(1969).
12. R. Gerdil and E. Luckon, *Helv, Chem. Acta.*, **44**, 1966(1961).
13. B. M. Mikhailov and A. N. Blokhina, *Izv. Akad. Nank SSSR, Ser. Khim.*, 164(1949); *Chem. Abstr.*, **44**, 2962(1950).
14. D. Walker and J. D. Hiebert, *Chem. Rev.*, **67**, 153(1967).
15. K. Wallenfels, G. Bachmann, D. Hofmann and R. Kern, *Tetrahedron*, 21, 2239(1965).
16. R. Mechoulam, B. Yagnilinsky, and YY. Gaoni. *J. Amer Chem. Soc.*, **90**, 2418(1968).