BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 1433—1440 (1968)

Kinetic Studies of Solvolysis. XV.*[1] Racemization Caused by the Molecular-Complex Formation in the Acetolysis of Optically Active 2,4,7-Trinitro-9-fluorenyl (+)-Camphor-10-sulfonate

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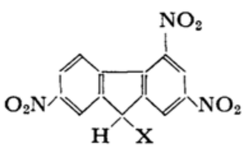
(Received December 26, 1967)

Optically active 2,4,7-trinitro-9-fluorenyl (+)-camphor-10-sulfonate (II) has been synthesized by asymmetric attack of (+)-camphor-10-sulfonic acid to 9-diazo-2,4,7-trinitrofluorene. Acetolysis of II is accelerated by added phenanthrene, anthracene, and hexamethylbenzene at 116—120°C. This acceleration is attributed to molecular complex formation between II and these hydrocarbons. The complex formation has been examined by spectrophotometry or by the isolation of the crystalline complex of II. The acetolysis product, *i. e.,* optically active 2,4,7-trinitro-9-fluorenyl acetate (III), has been racemized in the greater degree in the presence of the more aromatic hydrocarbons. This racemization is ascribed to the prolonged life of the S_N1 ion-pair intermediate caused by the rapid equilibration between the uncomplexed and the complexed S_N1-intermediate; the kinetic nature of this interaction has been discussed.

In the previous papers of this series[1] we have reported on several examples of the solvolysis of α-phenylethyl chloride which proceeded with net retention of configuration. With regard to these retentive solvolyses, it was not clear whether the "back-side shielding"[2] of the S_N1 solvolysis intermediate by a molecule of such retentive solvents as phenol[1a-c] and acrylonitrile[1d] was responsible for those retentive courses or not. In connection with this problem, we undertook the examination of the steric course for the acetolysis of a molecular complex formed from an aromatic hydrocarbon and an optically active substrate, because this reaction might be a model solvolysis which proceeds with net retention of the configuration possibly due to "back-side" shielding of the S_N1 intermediate by such aromatic hydrocarbons.

As a solvolysis substrate which exhibits facile complexation with some aromatic hydrocarbons, we chose a 2,4,7-trinitro-9-fluorenyl system, since Colter and his collaborators[3] clearly established that 2,4,7-trinitro-9-fluorenyl *p*-toluenesulfonate (I) forms a molecular complex with such aromatic hydrocarbons as phenanthrene, anthracene and hexamethylbenzene, and that the rate of the acetolysis of I is enhanced by this molecular complexation.



I : X = *p*-toluenesulfoxy
II : X = (+)-camphor-10-sulfoxy
III : X = acetoxy

The 2,4,7-trinitro-9-fluorenyl system with optical activity, caused by an asymmetric carbon at the 9-position, was prepared by an asymmetric attack of (+)-camphor-10-sulfonic acid to 9-diazo-2,4,7-trinitrofluorene; the complexation of 2,4,7-trinitro-9-fluorenyl (+)-camphorsulfonate (II) so synthesized was examined by spectrophotometry and by the isolation of the molecular complexes in the cases of phenanthrene and anthracene; then the kinetic measurements and the product analyses were attempted of II in the presence of those aromatic hydrocarbons.

It is the purpose of the present report to show that the acetolysis of II is accelerated in the presence of the aromatic hydrocarbons as it was found in the case of the acetolysis of I,[3] and that, contrary to our anticipation, the acetolysis involves inversion

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*[1] Presented at the 20th Annual Meeting of the Chemical Society of Japan, Tokyo, March 1967; Abstract III, p. 13. Part XIV of this series: Ref. 1c.

[1] a) Part XI: K. Okamoto, H. Yamada, I. Nitta and H. Shingu, This Bulletin, **39**, 299 (1966); b) Part XIII: K. Okamoto, M. Hayashi, K. Komatsu and H. Shingu, *ibid.,* **40**, 624 (1967); c) Part XIV: K. Okamoto, K. Komatsu and H. Shingu, *ibid.,* **40**, 1677 (1967); d) K. Okamoto, K. Komatsu and H. Shingu, *ibid.,* **39**, 2785 (1966).

[2] a) W. von E. Doering and H. H. Zeiss, *J. Am. Chem. Soc.,* **75**, 4733 (1953); b) A. Streitwieser, Jr., and W. D. Schaeffer, *ibid.,* **79**, 6233 (1957); c) A. Streitwieser, Jr., and S. Andreades, *ibid.,* **80**, 6553 (1958); d) H. Weiner and R. A. Sneen, *ibid.,* **87**, 287, 292 (1965); e) N. Kornblum and D. E. Hardies, *ibid.,* **88**, 1707 (1966).

[3] a) A. K. Colter and S. S. Wang, *ibid.,* **85**, 114 (1963); b) A. K. Colter, S. S. Wang, G. H. Megerle and P. S. Ossip, *ibid.,* **86.**, 3106 (1964).

of configuration, accompanied by predominant racemization, in the presence of those hydrocarbons; the mechanistic implications of the kinetic and the steric characteristics of these acetolyses have been discussed.

Results and Discussion

Optically Active 2,4,7-Trinitro-9-fluorenyl (+)-Camphor-10-sulfonate (II). A mixture of 9-diazo-2,4,7-trinitrofluorene[4] and (+)-camphor-10-sulfonic acid in nitromethane was allowed to react for 2 hr at 40°C. The desired 2,4,7-trinitro 9-fluorenyl (+)-camphor-10-sulfonate (II), $[\alpha]_D^{16}$ $+24.45°$, was obtained in a fair yield. The sulfonate II was converted to the optically-active 2,4,7-trinitro-9-fluorenyl acetate (III), $[\alpha]_D^{20}$ $-6.21°$, in good yields after 20 hr of reflux in acetic acid. This indicates that the attack of (+)-camphor-10-sulfonic acid to the 9-diazofluorene had been made asymmetrically, namely, that the optical activity of the sulfonate II was originated partly from a carbon atom at 9-position of 2,4,7-trinitro-9-fluorenyl group, besides from the original (+)-camphor-10-sulfonyl group.

Since under a basic condition, *e. g.*, in pyridine, the sulfonate II and the acetate III were led to highly colored materials from which neither pure starting materials nor identifiable products could be obtained, the usual optical resolution through the hydrogen phthalate of 2,4,7-trinitro-9-fluorenol was not undertaken. Furthermore, in the S_N2 reaction with sodium acetate in nitromethane, the sulfonate II did not afford the acetate III, but colored materials. This made difficult to confirm the relationships between the optical rotations and the configurations with respect to II and III (*vide infra*).

Formation of Crystalline Molecular Complexes of the Sulfonate II. The formation of crystalline molecular complexes involving some aromatic hydrocarbons and 2,4,7-trinitro-9-fluorenyl *p*-toluene-sulfonate (I) has been reported by Colter and Wang.[4] According to their methods, the complex forming properties of the sulfonate II were investigated briefly in the present work. The crystalline molecular complexes between II and phenanthrene (or anthracene), which formed from the benzene or nitromethane solution, are described in Table 1. The isolation of the complex between II and hexamethylbenzene, using benzene or nitromethane as the solvent, was unsuccessful.

TABLE 1. COMPLEXES OF AROMATIC HYDROCARBONS WITH 2,4,7-TRINITRO-9-FLUORENYL (+)-CAMPHOR-10-SULFONATE (II)

Aromatic hydrocarbon	Melting point °C, corr.	Color	Analysis N%	
			Found	Calcd
Phenanthrene	145.0—146.0	Yellow	5.73	5.92
Anthracene	149.0—149.5	Red	5.25	5.92

Spectrophotometric Studies of the Formation of Molecular Complexes of the Sulfonate II. On the assumption of 1 : 1 complex-formation in the solution, the complex-formation between the sulfonate II and aromatic hydrocarbons was investigated spectrophotometrically in glacial acetic acid at 24°C. The procedure of Colter and his collaborators[3b] was followed; optical densities of four to five mixtures of II $(18.4-8.84\times10^{-4}\,\text{M})$ and various aromatic hydrocarbons (*i. e.*, hexamethylbenzene $(1.55-2.65\times10^{-2}\,\text{M})$, phenanthrene $(1.25-5.00\times10^{-2}\,\text{M})$), and anthracene $(0.828-1.375\times10^{-3}\,\text{M})$ were measured at 400 and 410 mμ (or at 450 and 475 mμ for anthracene). The data were treated using Eq. (1),[5,6]

$$\frac{[\mathrm{A}]_0}{E_\lambda-\varepsilon_\lambda^{\mathrm{A}}[\mathrm{A}]_0}=\frac{1}{\varepsilon^{\mathrm{D\cdot A}}-\varepsilon_\lambda^{\mathrm{A}}}+\frac{1}{K_{\mathrm{T}}[\mathrm{D}]_0(\varepsilon_\lambda^{\mathrm{D\cdot A}}-\varepsilon_\lambda^{\mathrm{A}})} \tag{1}$$

$[\mathrm{A}]_0$ and $[\mathrm{D}]_0$ are the stoichiometric concentrations of II and an aromatic donor hydrocarbon; $\varepsilon_\lambda^{\mathrm{A}}$ and $\varepsilon_\lambda^{\mathrm{D\cdot A}}$ are the molar extinction coefficients of the sulfonate II and the 1 : 1 complex; E_λ is the measured optical density of the mixture, and K_{T} is the equilibrium constant for the reaction $\mathrm{A}+\mathrm{D}\rightleftarrows\mathrm{A\cdot D}$.

From the plots of $[\mathrm{A}]_0/(E_\lambda-\varepsilon_\lambda^{\mathrm{A}}\mathrm{A})$ *vs.* $1/[\mathrm{D}]$, the K_{T}'s and $\varepsilon_\lambda^{\mathrm{D\cdot A}}$'s were estimated. The results are listed in Table 2.

TABLE 2. THE K_{T} AND $\varepsilon_\lambda^{\mathrm{D\cdot A}}$ VALUES FOR 1 : 1 COMPLEX FORMATION BETWEEN II AND AROMATIC HYDROCARBONS IN ACETIC ACID AT 24.0°C

Aromatic hydrocarbon	Wavelength mμ	$\varepsilon_\lambda^{\mathrm{D\cdot A}}$ $\mathrm{M^{-1}cm^{-1}}$	K_{T}[a] $\mathrm{M^{-1}}$	
Hexamethyl-benzene	400	1100	2.4	Av. 2.6
	410	873	2.8	
Phenanthrene	400	2040	2.5	Av. 2.7
	410	1320	2.9	
Anthracene	450	425	4.6	Av. 4.1
	475	547	3.6	

a) Based on four measurements.

Rate Measurements and Product Analyses for Acetolyses of the Sulfonate II in the Presence of Aromatic Hydrocarbons. Acetolysis rates of the sulfonate II were measured at 116.3°C

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[4] A. K. Colter and S. S. Wang, *J. Org. Chem.*, **27**, 1517 (1962).

[5] The Ketelaar modification of the Benesi-Hildebrand equation:[6] J. A. A. Ketelaar, C. Van de Stolpe, A. Goudsmit and W. Dzcubas, *Rec. trav. chim.*, **71**, 1104 (1952).

[6] H. A. Benesi and J. H. Hildebrand, *J. Am. Chem. Soc.*, **71**, 2703 (1949).

TABLE 3. RATES OF ACETOLYSIS OF II IN THE PRESENCE OF AROMATIC HYDROCARBONS AT 116.3±0.5°C[a)]

Hexamethylbenzene		Phenancerene		Anthracene	
10^2[Hexa.][b)] M	$10^4 k_1$ sec^{-1}	10^2[Phena.] M	$10^4 k_1$ sec^{-1}	10^2[Anth.] M	$10^4 k_1$ sec^{-1}
0	0.75	0	0.75	0	0.75
5.11	1.42	4.10	1.34	2.06	5.04
7.49	1.74	5.46	1.54	3.00	6.40
8.56	1.82	7.55	1.79	4.05	8.16
9.22	1.92				

a) Initial concentrations of II were 2.75×10^{-5} M.
b) Concentrations were corrected for solvent expansion and referred to the temperature of the kinetic measurements.

TABLE 4. RESULTS OF ANALYSIS OF KINETIC DATA IN THE ACETOLYSIS OF II IN THE PRESENCE OF AROMATIC HYDROCARBONS

Aromatic hydrocarbon	$10^3 k_c$ sec^{-1} (116.3°C)	k_c/k_u[a)]	K_T M^{-1} (116.3°C)	K_T[b)] M^{-1} (24°C)
Hexamethylbenzene	1.5	20	1.0	2.6
Phenanthrene	1.3	18	1.2	2.7
Anthracene	2.9	39	8±4	4.1±3

a) $k_u = 7.5\times10^{-5}$ (sec^{-1}), at 116.3°C
b) Data from spectrophotometric measurements (see Table 2).

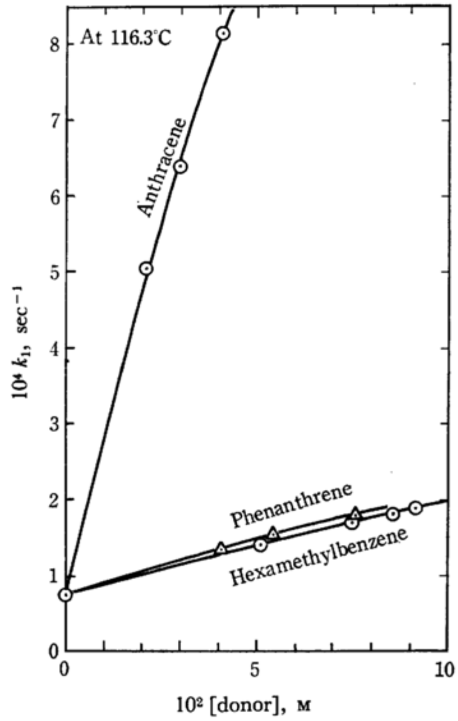

Fig. 1. Rates of acetolysis of II in the presence of aromatic hydrocarbons.

by following titrimetrically the liberated (+)-camphorsulfonic acid. The first-order rate constants, k_1's in the presence of the aromatic hydrocarbons are tabulated in Table 3 along with the rate constant in the absence of aromatic hydrocarbons. Plots of k_1 *vs.* the concentration of the added aromatic hydrocarbon are almost linear with gentle downward drift (see Fig. 1). This is a similar tendency to the observation made by Colter and Wang[3a)] on the acetolysis of the sulfonate I.

The product for the acetolysis of the sulfonate II, *i. e.*, the acetate III, was isolated in 85% yield after 20 hr of reflux of the reaction mixture. In the acetolyses in the presence of hexamethylbenzene, phenanthrene, or anthracene, were obtained some aromatic nitrohydrocarbons, along with the acetate III and unchanged aromatic hydrocarbons. Although the thorough characterization of these nitrohydrocarbons were not carried out, the hydrocarbons had rather high melting points and exhibited the infrared absorption bands characteristic for the nitro and the aromatic nucleus groups but no carbonyl absorption bands. From these facts the nitrohydrocarbons were assumed as the alkylated, *i. e.*, 2,4,7-trinitro-9-fluorenylated, products of the respective aromatic hydrocarbons.

The relation between the yields of the products and the initial concentrations of the added hydrocarbons is shown in Fig. 2 (see also Table 6). On the assumption mentioned above, the yields for nitrohydrocarbons were calculated as a monoalkylated product. The yields of the acetate III exhibit a decreasing tendency with increasing concentrations of added aromatic donor hydrocarbons, whereas the yields of monoalkylated aromatic hydrocarbons show an increasing tendency.

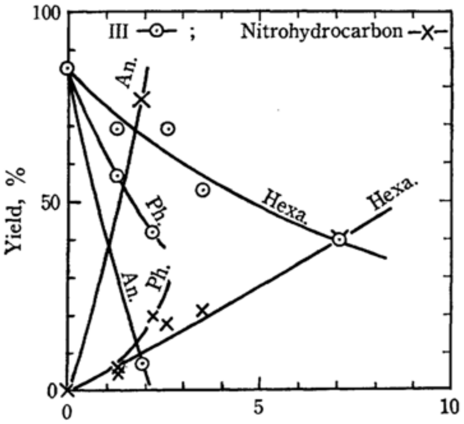

Fig. 2. Yields of III and nitrohydrocarbon in the acetolysis of II in the presence of aromatic hydrocarbons at a reflux temperature (Hexa. = hexamethylbenzene; Ph. = phenanthrene; An. = anthracene).

The latter tendency is enhanced in the case of the aromatic hydrocarbon with more facile complexing character (see the values of K_T's in Table 4).

Estimation of the Specific Rate for Complexed and Uncomplexed Sulfonate II. Among possible mechanisms for the rate enhancement by added hydrocarbons, as the simplest and the most probable one we chose the mechanism proposed by Colter and his collaborators.³⁾ According to the following reaction scheme A, in which a slight modification is introduced on the original mechanism³⁾ with respect to the nature of the reaction products,

$$\begin{tikzcd}
\mathrm{RX} + \mathrm{D} \arrow[r, shift left, "K_T"] \arrow[d, "k_u", "\mathrm{HOAc}"'] & \mathrm{RX{\cdot}D} \arrow[l, shift left] \arrow[d, "k_c", "\mathrm{HOAc}"'] \\
\mathrm{ROAc} + \mathrm{D} \arrow[r, shift left, "K_A"] & \mathrm{ROAc{\cdot}D} \arrow[l, shift left] \\
+\,\mathrm{RD} + \mathrm{HX} & +\,\mathrm{RD} + \mathrm{HX}
\end{tikzcd}$$

Scheme A

(RX for II, ROAc for III, D for aromatic donor hydrocarbons, HX for (+)-camphorsulfonic acid, RD for alkylated hydrocarbons), the observed rate constant is given by the expression

$$k_{\mathrm{obsd}} = k_u F_u + k_c F_c \tag{2}$$

where F_u and F_c are fractions of II uncomplexed and complexed, respectively. Under experimental conditions where the hydrocarbon concentration $[\mathrm{D}]_0$ is greater than the complex concentration $\{[\mathrm{RX{\cdot}D}]+[\mathrm{ROAc{\cdot}D}]\}$, we obtain the Colter's expression (Eq. (3)).

$$\frac{1}{(k_{\mathrm{obsd}}-k_u)} = \frac{1}{(k_c-k_u)} + \frac{1}{K_T[\mathrm{D}]_0(k_c-k_u)} \tag{3}$$

A plot of $1/(k_{\mathrm{obsd}}-k_u)$ *vs.* $1/[\mathrm{D}]_0$ for the acetolysis in the presence of anthracene at 116.3°C is shown in Fig. 3, and the results of analysis of kinetic data for the respective aromatic hydrocarbons are tabulated in Table 4.

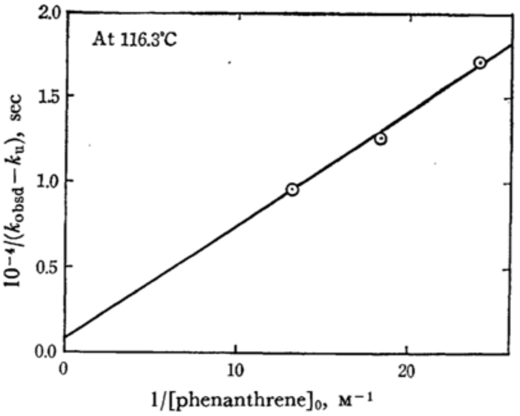

Fig. 3. Plot of $10^{-4}/(k_{\mathrm{obsd}}-k_u)$ *vs.* 1/[phenanthrene].

Except the case of anthracene where only rough estimation of the K_T was made due to a large experimental error, the two sets of K_T's *i. e.*, K_T's from kinetic and spectrophotometric data, show a fair agreement with each other.

The values of the rate constant for the complexed substrate, k_c, are greater than those of the rate constant for the uncomplexed substrate, k_u (Table

TABLE 5. ESTIMATION OF THE AMOUNTS OF THE PRODUCTS FORMED FROM THE COMPLEXED AND UNCOMPLEXED SUBSTRATE IN THE ACETOLYSIS OF II IN THE PRESENCE OF HEXAMETHYLBENZENE AT 116.3°C[a)]

10^2[Hexa.] M	Equilibrium composition		Product[b)] composition from	
	Complexed II	Uncomplexed II	Complexed II	Uncomplexed II
0.00	0.00%	100%	0.00%	100%
1.30	1.27	98.7	22.2	77.8
2.61	2.59	97.4	34.7	65.3
3.47	3.31	96.7	40.7	59.3
7.11	6.54	93.5	58.3	41.7

a) Initial concentration of II = 1.30×10^{-2} M ; $K_T = 1.0$ (M^{-1}) ; $k_c/k_u = 20$.
b) III and nitrohydrocarbon (see text).

Table 6. Optical rotations of III and the yields of the products in the acetolysis of II in the presence of aromatic hydrocarbons at the reflux temperature (116—120°C)

Aromatic hydrocarbon	10^2 [Arom.] M	III		Nitrohydrocarbon
		% yield	$[\alpha]_D$ in $MeNO_2$	% yield
None	0.00	85	$-6.2\pm0.3°$	—
Hexamethylbenzene	1.30	69	$-1.6\pm0.3°$	6
	2.61	69	$-0.4\pm0.3°$	18
	3.47	53	$-0.8\pm0.7°$	21
	7.11	40	$-0.9\pm0.6°$	41
Phenathrene	1.30	57	$-4.4\pm0.5°$	4
	2.18	42	$-2.2\pm1.0°$	20
Anthracene	1.93	7	—	77

a) Initial concentration of II ($[\alpha]_D$ +24.45°) was 1.30×10^{-2} (M).
b) See text.

4); this rate increase for the complexed substrate is elucidated as due to the neutralization of the electron-withdrawing effect of the nitro substituents on the sulfonate II by complexation with the electron-donating aromatic hydrocarbon, since the nitro group on the substrate is known as a retarding substituent of the S_N1 solvolysis rate.

On the basis of the scheme A, we can calculate the respective amounts of the solvolysis products formed from the complexed substrate, RX·D, and the uncomplexed substrate, RX, using the estimated values for K_T, k_c and k_u. The results for the case of hexamethylbenzene are shown in Table 5, along with the equilibrium compositions for the complexed and uncomplexed substrate under the respective reaction conditions.

Optical Rotations of the Acetate III Obtained in the Presence of Aromatic Hydrocarbons. Figure 4 shows relationships between the optical rotations of the acetate III and the initial concentrations of aromatic hydrocarbons. The optical rotations of the acetate III decrease with an increase of the added hexamethylbenzene concentration; at the higher concentrations the optical rotations exhibit a tendency to a complete loss of the optical activity. In a similar fashion, optical rotations of the acetate III show a rapid decrease with an increase of the amounts of added phenanthrene (Fig. 4).

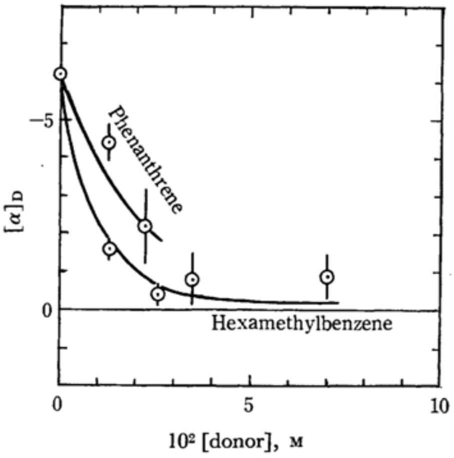

Fig. 4. Optical rotations of III formed in the acetolysis of II in the presence of aromatic hydrocarbons at reflux temperature.

As is mentioned above, an S_N2 reaction of the sulfonate II, which was carried out to determine the configurations of the sulfonate II or the acetate III, was unsuccessful owing to the unstability of II or III under the basic reaction condition. However, in acetolysis of a simple secondary alkyl substrate, the inversion of the configuration accompanying some racemization is usually observed, and this inversion is considered as a general character for the steric course of the solvolysis of simple alkyl compounds.[7] Accordingly, we may consider that the acetolysis of the sulfonate II also proceeds with net inversion of configuration.

If the greater S_N1 rate constant for the complexed substrate, as is compared with that for the uncomplexed sulfonate II, reflects on the prolonged life for the 2,4,7-trinitro-9-fluorenyl cation produced as the S_N1 intermediate, this longer life of the intermediate may cause the greater extent of racemization in the product III.

The Estimation of the Extents of Racemization of the Acetate III on the Basis of the Reaction Scheme A. In view of the complete racemization of III formed in the presence of added hexamethylbenzene, we may assume that the acetate III produced through the complexed substrate has no optical activity, and that, on the other hand, the uncomplexed substrate affords the acetate III with an optical rotation ($[\alpha]_D$ −6.2°) under the same reaction conditions.

On the basis of this assumption, the predicted values for the optical rotation of the acetate III can be calculated from the reaction scheme A, using the value for the product composition (*cf.*

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[7] See the footnote 1 of the Ref. 1b.

TABLE 7. COMPARISON OF THE OPTICAL ROTATIONS OF III FORMED IN THE ACETOLYSIS OF II IN THE PRESENCE OF VARIOUS AMOUNTS OF HEXAMETHYLBENZENE AT THE REFLUX TEMPERATURE (116—120°C)[a]

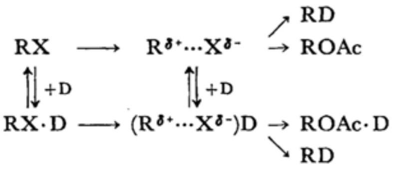
10^2 [Hexa.]	$[\alpha]_D$ of III Observed	$[\alpha]_D$ of III Calculated, based on the reaction scheme A[b]
0.00	−6.2°	—
1.30	−1.6°	−4.8°
2.61	−0.4°	−4.0°
3.47	−0.8°	−3.7°
7.11	−0.9°	−2.6°

a) Initial concentration of II were 1.30×10^{-2} (M).

b) $[\alpha]_{D\,\mathrm{calcd}} = -6.2° \times$[%, Product from the uncomplexed II]/100.

Table 5). Since the actual products contain some nitrohydrocarbon, and since the S_N1 intermediate, which is formed from a complexed substrate, may afford much more nitrohydrocarbon than the uncomplexed intermediate, this prediction from the scheme A (Table 7) may be somewhat lower estimation.

Table 7 shows that the observed optical rotations for III are substantially lower than the values calculated on the basis of the scheme A. This gap clearly indicates that the aromatic hydrocarbon makes an additional contribution, other than the complexation of the substrate, to the loss of the optical activity of the acetate III. Therefore, we may add to the reaction scheme A an interconversion course between the complexed and uncomplexed S_N1 intermediate in order to explain this excess of racemization in the acetate. This is shown in the scheme B.



Scheme B

Kinetic Nature of the Interaction between the Aromatic Hydrocarbon and the S_N1 Intermediate. It may be difficult to find an unambiguous elucidation of the reason why the interconversion between the complexed and the uncomplexed intermediate causes the excess of the racemization for the acetate III. However, as one of the possible explanations, we may suggest the following mechanism.

The association and dissociation rates in the equilibrium between the complexed and the uncomplexed intermediate would be so frequent that the attack of the nucleophilies, *i. e.*, acetic acid or the acetate ion, would relatively be hindered. Consequently, the life of the ion-pair intermediate is prolonged and the cationic part of the intermediate rotates[8] more frequently until its asymmetric center is attacked by the nucleophile. This means that the intermediate would be racemized in greater extent in the presence of aromatic donor hydrocarbons.

Furthermore, the rate of the nucleophilic attack on the complexed intermediate would be lower than the rate for the uncomplexed intermediate, and accordingly the more acetate III (inverted) may be produced from uncomplexed intermediates than complexed ones. Thus, even if the nucleophilic attack on the complexed intermediate were made from the front-side, resulting in the retention of the configuration of the acetate, the predominance of the acetate produced from the inversive attack on the uncomplexed intermediate would lead to the over-all net inversion of configuration of the acetate. If this is the case in our experiments, it would be unable to verify whether the retentive attack is predominant for the complexed intermediate or not.

Experimental

Materials. Phenanthrene (mp 100.7—101.5°C, corr.) was purified according to the method of Phillips[9] by refluxing a mixture of phenanthrene, maleic anhydride, and xylene, and by succeeding recrystallization from ethanol; anthracene (mp 219.5—221.0°C, corr.) was recrystalized from acetic acid and then chromatographed over basic alumina, using benzene as an eluent. Hexamethylbenzene (mp 166.9—168.4°C, corr.) was used as received. Acetic acid (bp 118.0—118.5°C) was purified by refluxing with a small amount of acetic anhydride and by subsequent fractional distillation.

9-Diazo-2,4,7-trinitrofluorene (mp 204—205°C, decomp.) was prepared by the method described by Colter and Wang.[4] (+)-Camphor-10-sulfonic acid (mp 201°C, corr.; $[\alpha]_D^{20}$ +40.5° (*c* 3.16, ethanol)) was recrystallized from ethyl acetate.

The Asymmetric Synthesis of Optically Active 2,4,7-Trinitro-9-fluorenyl (+)-Camphor-10-sulfonate (II). A mixture of 9-diazo-2,4,7-trinitrofluorene (13.0 g, 0.0397 mol) and (+)-camphor-10-sulfonic acid (13.0 g, 0.0559 mol) in nitromethane (350 cc) was placed in a 500-cc three-necked flask equipped with a thermometer, a drying tube, and a magnetic stirrer. After 2 hr of stirring at 40°C, the reaction mixture was washed with two 100-cc portions of 10% aqueous sodium chloride and then with two 100-cc portions of water. Concentration of the nitromethane solution afforded bright yellow crystals (13.64 g). After recrystallization from 40 cc of nitromethane, 11.29 g (53.6%) of II (mp 192.0—193.0°C, decomp., corr.;

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[8] K. Okamoto, N. Uchida, S. Saitô and H. Shingu, This Bulletin, **39**, 307 (1966).

[9] D. D. Phillips in "Organic Syntheses," Coll. Vol. IV, p. 313 (1963).

$[\alpha]_D^{16}$ +24.45±0.4° (*c* 2.12, nitromethane)) was obtained.

Found: C, 51.78; H, 4.05%. Calcd for $C_{33}H_{21}O_{10}N_3S$: C, 51.98; H, 3.98%.

The Acetolysis of II in the Absence of Added Aromatic Hydrocarbons. A mixture of II (0.600 g, 0.00113 mol) and acetic acid (81 cc) was refluxed for 20 hr in a 200-cc round-bottomed flask equipped with a reflux condenser and a drying tube. After evaporation of acetic acid in vacuo, the residual yellow crystals were washed with water, ethanol, and ether, leaving 0.340 g (85%) of 2,4,7-trinitro-9-fluorenyl acetate (III) (mp 234—236°C, decomp. (lit.[4]) mp 235°C, decomp.); $[\alpha]_D^{20}$ −6.21±0.5° (*c* 2.13, nitromethane)).

The Acetolysis of II in the Presence of Added Aromatic Hydrocarbons. In a similar fashion to the acetolysis in the absence of added aromatic hydrocarbons, a mixture of II, an aromatic hydrocarbon and acetic acid was refluxed in a 200-cc three-necked flask equipped with a reflux condenser and a thermometer. After an appropriate reaction time, acetic acid was evaporated *in vacuo,* and the reaction products were isolated by extraction or by recrystallization. The details of the experimental procedures for some representative runs are cited below.

The Acetolysis of II in the Presence of Hexamethylbenzene. A mixture of II (1.00 g, 0.00188 mol), hexamethylbenzene (0.612 g, 0.0037 mol), and acetic acid (135 cc) was refluxed for 19 hr at 120°C. After evaporation of acetic acid *in vacuo* at 50—60°C, the residual yellow solid was washed with 80 cc of water and with 80 cc of ether to remove the remaining acetic acid and the unchanged hexamethylbenzene. The crude yellow crystals (0.551 g) was dissolved in 15 cc of hot nitromethane; after being kept at room temperature, the solution deposited bright yellow crystals (0.140 g; 18% yield, calculated as an alkylated hexamethylbenzene, *vide infra;* mp 279—280.5°C, decomp., corr.). After three recrystallizations of these crystals from nitromethane, 0.030 g of crystals (mp 293.7°C, decomp., corr.) were obtained (Found: C, 64.30; H, 4.98; N, 8.14%. Calcd for $C_{24}H_{21}O_6N_8$: C, 64.42; H, 4.73; N, 9.39%). These purified crystals exhibited infrared absorptions at 1520 and 1345 cm^{-1} (NO_2), at 2920 cm^{-1} (CH_3), at 3150 and 810 cm^{-1} (aromatic C–H). No carbonyl absorption was exhibited in the range 1650—1800 cm^{-1}. Although no further characterization was carried out, we assumed these crystals as an aromatic nitrohydrocarbon produced from hexamethylbenzene and II. The mother liquors obtained from the recrystallization of the above mentioned crude crystals were condensed to 5 cc, and 0.407 g (69%) of III (mp 231—234°C, uncorr.; the identical infrared spectrum with that of the authentic sample; $[\alpha]_D^{20}$ −0.42±0.3° (*c* 1.79, nitromethane)) was obtained.

The Acetolysis of II in the Presence of Phenanthrene. A mixture of II (1.00 g, 0.00188 mol), phenanthrene (0.337 g, 0.001885 mol), and acetic acid (135 cc) was refluxed at 120°C for 17 hr. After evaporation of acetic acid *in vacuo* at 50—55°C, and washing with water, 0.739 g of yellow crystals were obtained. These crystals were refluxed with 15 cc of ether, leaving 0.49 g of a yellow solid; this was dissolved in 15 cc of nitromethane. After standing overnight in an ice-box, 0.033 g (4.2% yield, calculated as trinitrofluorenylphenanthrene, *vide infra*) of bright yellow crystals (mp 273.5—275.0°C, uncorr.) were obtained. Four recrystallizations of these crystals from nitromethane afforded 0.010 g of bright yellow needles (mp 297.5—298.5°C), which infrared spectra had characteristic bands at 3100 and 740 cm^{-1} (aromatic C–H) and at 1525 and 1345 cm^{-1} (NO_2). No carbonyl bands was found in the spectra (Found: C, 62.49; H, 3.29; N, 9.55%. Calcd for $C_{27}H_{15}O_6N_3$: C, 67.92; H, 3.17; N, 8.80%). Although results of elemental analysis were not satisfactory, we considered these crystals as trinitrofluorenylphenanthrene from the high melting point and the characteristic bands of the infrared spectra. After being condensed to 5 cc, the filtrate from the nitromethane solution of the crude reaction products afforded 0.399 g (57.2%) of III (mp 227—229°C, uncorr.; $[\alpha]_D^{22}$ −4.37±0.44° (*c* 1.71, nitromethane); the same infrared spectrum as the authentic sample).

The Acetolysis of II in the Presence of Anthracene. A mixture of II (0.500 g, 0.000943 mol), anthracene (0.250 g, 0.00140 mol), and acetic acid (62.5 cc) was refluxed for 10.3 hr. After evaporation of acetic acid *in vacuo* at 50—60°C, the residual red-brown solid was washed with water. The dried solid was dissolved in 10 cc of acetone, leaving 0.240 g (53.4% yield, calculated as trinitrofluorenylanthracene) of insoluble crystals. After five recrystallizations from nitromethane, 0.050 g of orange needles (mp 294.0—294.5°C, uncorr.; Found: C, 67.09; H, 3.14; N, 8.19%. Calcd for $C_{27}H_{15}O_6N_3$: C, 67.92; H, 3.17; N, 8.80%). The infrared spectra had characteristic bands at 3110 and 730 cm^{-1} (aromatic C–H), 1520 and 1340 cm^{-1} (NO_2); No carbonyl bands were found. After condensation of the filtrate from the 10 cc of acetone solution, 0.105 g (23.4% yield, calculated as trinitrofluorenylanthracene) of the second crop (mp 305°C, corr., red-orange needle after four recrystallizations; the same infrared spectrum as the first crop) was obtained. From the mother liquors 0.165 g of a mixture of anthracene and III was obtained; the composition was determined by elution chromatography over acidic alumina. Anthracene (0.067 g) was eluted with benzene, and 0.025 g (7%) of III (mp 208—216°C, uncorr.; the same infrared spectrum as the authentic sample) was obtained from the succeeding fractions using ether as an eluent.

Isolation of Crystalline Molecular Complexes of II. To the solution of II (0.176 g, 0.000331 mol) in benzene (6 cc) was added anthracene (0.067 g, 0.000376 mol), resulting in a deep red solution. After standing overnight at room temperature, the red needles were collected by filtration, washed with small portions of ether. The dried complexes melted at 149.0—149.5°C (corr.) and weighed 0.11 g (0.000155 mol).

Found: C, 63.81; H, 4.96; N, 5.25%. Calcd for $C_{37}H_{31}O_{10}N_3S$: C, 62.62; H, 4.40; N, 5.92%.

From a mixture of II (0.305 g, 0.000575 mol) and phenanthrene (0.102 g, 0.000573 mol) in 3 cc of nitromethane, 0.120 g (0.000169 mol) of bright yellow complexes (mp 145.0—146.0°C, corr.) were obtained after standing overnight at room temperature.

Found: C, 62.64; H, 4.11; N, 5.73%. Calcd for $C_{37}H_{31}O_{10}N_3S$: C, 62.62; H, 4.40; N, 5.92%.

A trial to obtain the complexes between hexamethylbenzene and II from the benzene or nitromethane solution of a mixture (1 : 1 mol) of these components was unsuccessful.

Kinetic Measurements. All kinetics were measured at 116.4±0.5°C. The reaction vessels were 50-cc measuring flasks, and about 40 cc of the reaction mixture was placed. The first aliquot (3 cc) was removed 10 min after setting the flask in a thermostat. The subsequent aliquots (3 cc for each) were removed at intervals, added into 1 cc of cooled sodium acetate solution (0.01 N) in acetic acid, and titrated with 0.01 N perchloric acid in acetic acid, using crystal violet as an indicator. All the data were treated graphically by a plot of log $a/(a-x)$ against the time. In each run the reaction was followed to at least 80% conversion, and a smooth linear relationship was obtained for each run.

Spectrophotometric Determination of K_T. Optical density measurements were carried out with a double set of thermospacers connected to a circulating constant temperature bath. The temperature of the cell compartment was held in this way at 24.0±0.2°C. The measurements were carried out at the range of 390 to 600 mμ, using quartz cells with a path length of 10 mm. The data were treated in the manner described in text.