Reaction of Tropylium Ion with Tropolone[1]

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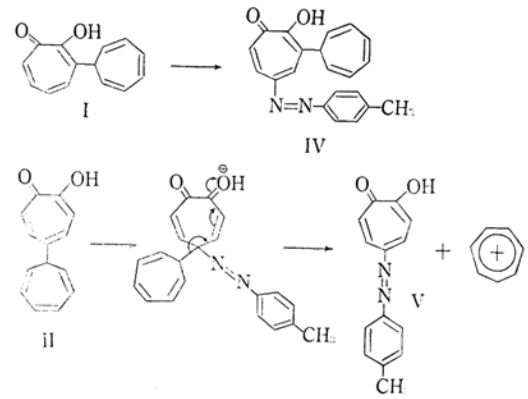
In a previous paper[2] the authors reported on the reaction of tropylium ion with β-naphthol. Since tropolone is regarded as a compound analogous to phenols in its chemical behavior, especially toward electrophilic reagents,[3] it is to be expected that a reaction would take place between tropylium ion and tropolone. The present paper will describe this reaction and the structure and reactions of the products obtained.

The reaction of equimolecular amounts of tropylium bromide and sodium salt of tropolone affords three kinds of acidic substances with recovery of tropolone. They are yellowish needles, (I) $C_{14}H_{12}O_2$ (m. p. 89°C), (II) $C_{14}H_{12}O_2$ (m. p. 127°C) and (III), $C_{21}H_{18}O_2$ (m. p. 137°C), which were obtained in 20, 18 and 36% yields respectively. From their analytical values, the red coloration with ferric chloride, which is characteristic of tropolone derivatives, and a consideration of the preferential attack of the electrophilic reagent at the 3- and 5-positions of the tropolone ring, I and II have been assumed to be 3- or 5-(7-tropyl)tropolone. The coupling of I with *p*-toluenediazonium chloride results in the formation of a crystalline azo dye (IV) $C_{21}H_{18}O_2N_2$ (m. p. 159°C), which indicates that I is 3-(7-tropyl)tropolone with no substituent at the 5-position.[4] II also affords an azo dye (V) $C_{14}H_{12}O_2N_2$ (m. p. 200°C) by coupling with *p*-toluenediazonium chloride. However, its analytical value reveals that the tropyl group of the 5-position of II would be replaced by the *p*-tolylazo group. In fact, V is found to be identical with the known 5-(*p*-tolylazo)tropolone[5] by a comparison of their infrared absorption spectra; there is no depression of their mixed melting point. Since the reaction is considered to proceed as depicted below, II is certainly 5-(7-tropyl)tropolone. There are some examples of the same type of replacement reaction in tropolone derivatives; that is, the 5-hydroxymethyl[6] and 5-morphorinomethyl groups[6] at the 5-position are replaced with the *p*-tolylazo group.



As Figs. 1, 2 and 3 show, the ultraviolet spectra and nuclear magnetic resonance spectra[7] of I and II support the correctness of the structure of I and II. In their nuclear magnetic spectra, I and II exhibit five groups of signals, a, b, c, d and e, which have intensity ratios corresponding to 1, 2, 4, 4 and 1 protons respectively. The triplet signal, a, the quartet, b and the multiplet, c, are ascribed to the C_7, $C_{1,6}$ and $C_{2,3,4,5}$ protons of the tropyl group, and d and e are attributed to the tropolone-ring proton and that of the hydroxyl group respectively. The symmetrical signal d of II is especially characteristic of the A_2B_2 system,[8] indicating II to be 5-(7-tropyl)tropolone. The e signal shifts to a lower field when one drop of acetic acid is added.

The acidic compound III couples with *p*-toluenediazonium salt in pyridine, affording an azo dye (VI) $C_{28}H_{24}O_2N_2$ (m. p. 188°C). III also gives a crystalline sodium salt and a hydrazine salt which readily regenerates III on acidifying. From these facts and from the

1) Presented at the 14th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1961.

2) T. Nozoe, S. Ito and T. Tezuka, *Chem. & Ind.*, **1960**, 1088; T. Nozoe, T. Mukai, S. Ito and T. Tezuka, to be published.

3) T. Nozoe et al., "Comprehensive Organic Chemistry" (Daiyuki-Kagaku), Vol. 13, Asakura Publishing Co., Tokyo (1960), p. 124.

4) In general, it is known that tropolone derivatives with a substituent at the 5-position do not give an azo dye in the crystalline state. This method is often used for the diagnosis of the existence of a 5-substituent.

5) T. Nozoe, S. Seto, Y. Kitahara, M. Kunori and Y. Nakayama, *Proc. Japan Acad.*, **26**, (7) 38 (1950).

6) S. Seto and K. Ogura, This Bulletin, **32**, 493 (1959).

7) All NMR spectra were measured in the Laboratory of Professor Hazato of the Chemical Research Institute of Non-aqueous Solutions, Tohoku University.

8) L. M. Jackman, "Application of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry," Pergamon Press, London (1959), p. 92.

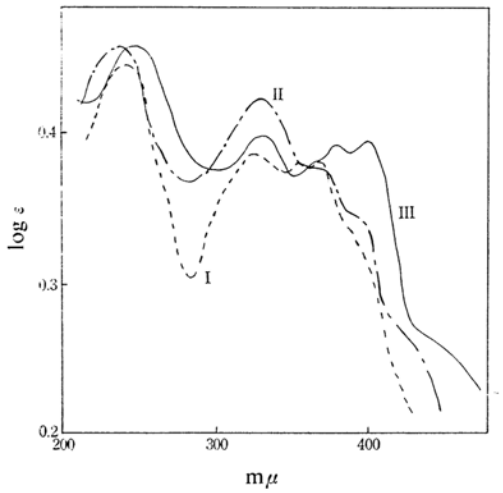
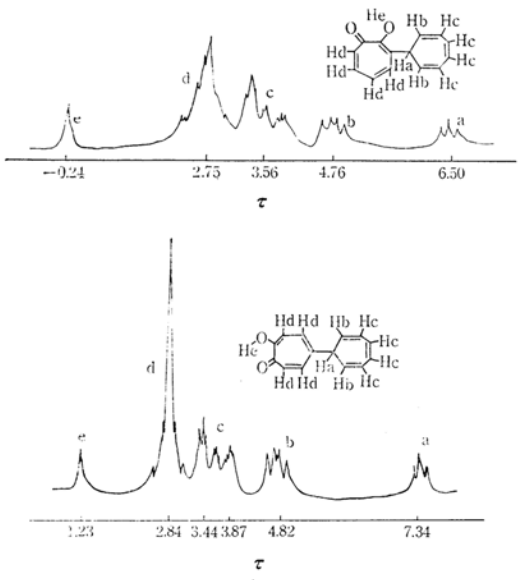
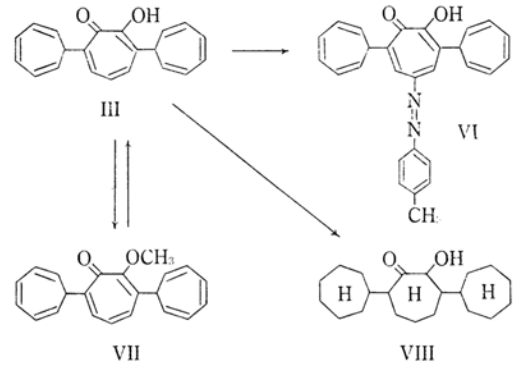


Fig. 1. UV spectra of I, II and III in methanol.



Figs. 2 and 3. NMR spectra of I and II in carbon tetrachloride (40 Mc.), with cyclohexane as an internal reference.

analytical value, III is assumed to be 3, 7-di-(7-tropyl)tropolone. The ultraviolet spectrum shown in Fig. 1 supports the assignment of III as a tropolone derivative. In the infrared spectrum, however, there is no absorption band due to the hydroxyl group and III does not show any coloration with ferric chloride in an organic solvent, such as benzene and chloroform; it does, however, show a red coloration in *n*-butanol. Since III is 3, 7-di(7-tropyl)tropolone, not a 3, 5-derivative, these abnormalities concerning the infrared spectrum and coloration can be understood from the steric hindrance of the tropyl groups situated in the 3- and 7-positions. Actually, III gives only one methyl ether (VII) (m. p. 86°C), upon being treated with diazomethane. Nine moles of hydrogen are absorbed when III is hydrogenated over platinum oxide, yielding a compound (VIII) $C_{21}H_{36}O_2$ (m. p. 60°C) which shows a band at 3500 cm^{-1} for a hydroxyl and at 1700 cm^{-1} for a carbonyl group.



The NMR spectrum of III, shown in Fig. 4, furnishes additional evidence concerning its structure. There are also five groups of absorption signals, a, b, c, d and e. The symmetrical shape of the a triplet which appears at 6.48τ, at almost the same field as a of I, supports the theory that the two tropyl groups are situated in equivalent positions, that is, the 3- and 7-positions. If they were not at equivalent positions, they would give rise to the double triplet in this region of field. The signal d at 2.69τ, ascribed to the tropolone-ring proton, shows AB_2 type coupling.[8] This fact also supports the idea that III is 3, 7-di-(7-tropyl)tropolone.

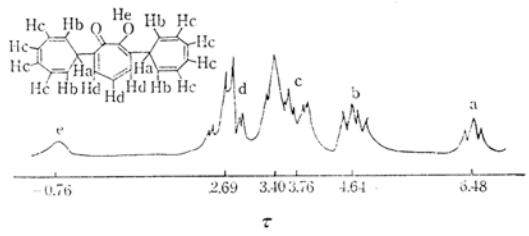
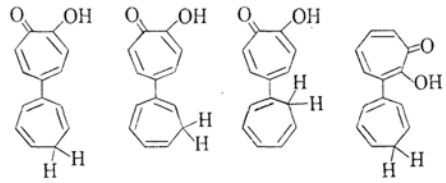


Fig. 4. NMR spectrum of III in carbon tetrachloride (40 Mc.), with cyclohexane as an internal reference.

The distillation of the mixture obtained from the reaction of tropylium ions and tropolone at the bath temperature of 180°C, before separating I, II and III, affords two additional acidic compounds; (IX) $C_{14}H_{12}O_2$ (m. p. 98°C) and (X) $C_{14}H_{12}O_2$ (m. p. 60°C). They are assumed to be isomeric monotropyltropolones resulting from a shift of the hydrogen during heating, because of their

analytical values and the red coloration with ferric chloride characteristic of tropolones. On coupling with *p*-toluenediazonium chloride, IX does not afford any crystalline azo compound, but X does afford an azo dye, (XI) $C_{21}H_{18}O_2N_2$ (m. p. 148°C).[4]



IXa IXb IXc X

This fact indicates that IX is 5- and that X is 3-tropyltropolone isomeric to II and I. In the case of IX, there are three possible formulas in which double bonds of the tropyl group are conjugated to the tropolone ring; IXa, IXb and IXc. In fact, the ultraviolet spectra of IX and X are shifted to a longer wavelength region than those of I and II, as Fig. 5 shows. However, IXc can be ruled out, because its NMR spectrum shows a triplet with the area of two protons at 7.71τ which is attributed to the C_7 proton of the tropyl group. Recently, ter Borg, Kloosterziel and Van Meurs[9] reported that 7-deuterocycloheptatriene, when heated at 100~140°C, rearranged to 3-deuterocycloheptatriene as a result of the 1, 5-transannular shift of hydrogen. Nozoe and his co-workers also reported that 7-tropylbenzene[10] and 4-(7-tropyl)phenol[11] rearranged to the corresponding 2 or 3-tropyl derivatives upon being heated with or without a base. According to ter Borg et al., IXa would be a more favorable formula than IXb, while X would have the similar isomeric formulas. It is necessary to do more detailed study in order to elucidate the structure of IX and X and to clarify the thermorearrangement of I, II and III. The results of this series of studies will be published in this Bulletin.

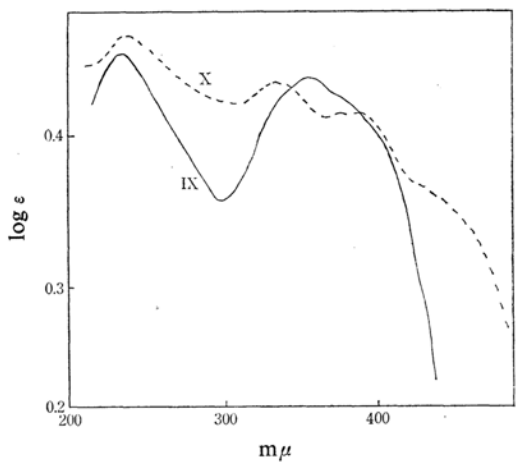


Fig. 5. UV spectra of IX and X in methanol.

Experimental[12,13]

The Reaction of Tropylium Bromide and Tropolone Sodium Salt: The Formation of 3-(7-Tropyl)- (I), 5-(Tropyl)- (II) and 3, 7-Di(7-tropyl)tropolone (III).—To a suspension of the sodium salt prepared from 10 g. of tropolone (0.0821 mol.) in 80 ml. of absolute ethanol, 13.6 g. (0.0795 mol.) of tropylium bromind were added. The reaction mixture was refluxed for 5.5 hr. After the sodium bromide had been filtered off, the evaporation of the solvent afforded 17 g. of an oil, which was found by paper chromatography to be a mixture of four kinds of tropolone derivatives. The fractional recrystallization of the sodium salt obtained from the oil from a water-ethanol mixture gave five fractions as follows. (1) The acidification of 2.8 g. of the most sparing soluble portion by 2 N hydrochloric acid afforded 2.2 g. of yellow crystals (m. p. 125~131°C), which on recrystallization from a benzene-ethanol mixture gave yellow needles (III) (m. p. 137°C). IR (KBr): no OH group, 1600, 1550 (C=O and C=C), 748, 695 cm^{-1} (7-tropyl group).[14]

Found: C, 83.44; H, 5.86. Calcd. for $C_{21}H_{18}O_2$: C, 83.42; H, 6.00%.

Treating III with hydrazine hydrate gave hydrazine salt (m. p. 160°C (decomp.)) as pale yellow needles.

Found: N, 8.80. Calcd. for $C_{21}H_{22}O_2N_2$: N, 8.38%.

(2) The acidification of 2.0 g. of the second sparing soluble portion afforded 1.2 g. of crystals (m. p. 60~65°C), the recrystallization of which from ethanol gave yellow needles (I) (m. p. 88~89°C). IR (Nujol): 3120 (OH), 1615, 1600, 1550 (C=O, C=C) 755, 704 cm^{-1} (7-tropyl group).[14]

Found: C, 79.25; H, 5.70. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

(3) The acidification of 2.3 g. of sodium salt afforded 1.1 g. of crystals (m. p. 100°C), the recrystallization of which from benzene gave yellow needles (II) (m. p. 126~127°C). IR (Nujol): 3200 (OH) 1615, 1550 (C=O and C=C) 755 and 704 cm^{-1} (7-tropyl group).[14]

Found: C, 79.69; H, 5.71. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

(4) The acidification of 1.6 g. of sodium salt afforded crystals (m. p. 40~45°C), which were identified as tropolone by a comparison of the infrared spectra.

9) A. P. ter Borg, H. Kloosterziel and N. Van Meurs, *Chem. & Ind.*, **1962**, 359.

10) T. Nozoe, T. Mukai, T. Tezuka and K. Osaka, *J. Chem. Soc. Japan. Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **83**, 662 (1963).

11) T. Nozoe and K. Kitahara, *Chem. & Ind.*, **1962**, 1192.

12) All melting points are uncorrected.

13) The microanalyses were carried out by Miss Ayako Iwanage and Mutsuko Suzuki in this Laboratory.

14) K. Conrow, *J. Am. Chem. Soc.*, **81**, 5461 (1959).

(5) The acidification of 1 g. of the most easily soluble portion afforded 0.85 g. of oil, which was not studied in more detail.

The Coupling of 3-(7-Tropyl)tropolone (I) with *p*-Toluenediazonium Chloride. The Formation of Azo Dye (IV).—To a solution of 60 mg. of I dissolved in 0.3 ml. of pyridine, an aqueous solution of *p*-toluenediazonium chloride prepared from 30 mg. of *p*-toluidine in the usual way was added drop by drop while the solution was cooled by ice. The reaction mixture was then stirred for 1 hr., diluted with water, and extracted with chloroform. After the mixture had been dried on sodium sulfate, the evaporation of the solvent afforded 90 mg. of red crystals (IV) with a melting point of 157 ~158°C after recrystallization from the benzene-ethanol mixture.

λ_{max}^{MeOH} mμ (log ε): 233 (4.13), 297 (3.88), 390 (4.37) and 440 (sh).

Found: C, 76.31; H, 4.25; N, 8.33. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.34; H, 5.49; N, 8.48%.

The Reaction of 5-(7-Tropyl)tropolone (II) with *p*-Toluenediazonium Chloride. The Formation of Azo Dye (V).—To a solution of 38 mg. of II dissolved in 0.2 ml. of pyridine, an aqueous solution of *p*-toluenediazonium chloride prepared from 15 mg. of *p*-toluidine was added drop by drop while the solution was being cooled by ice, and stirring was continued for 1.5 hr. The crystals precipitated were collected by filtration to give 25 mg. of red crystals (m. p. 145~150°C). Recrystallization from a benzene-ethanol mixture afforded orange needles (V) (m. p. 199~200°C), which were identified with authentic 5-(*p*-tolylazo)tropolone[5] by a comparison of their infrared spectra and by a mixed melting point determination.

The Coupling of 3,7-Di(7-tropyl)tropolone (III) with *p*-Toluenediazonium Chloride. The Formation of Azo Dye (VI). — To a solution of 100 mg. of sodium salt of III dissolved in 2 ml. of pyridine, an aqueous solution of *p*-toluenediazonium chloride prepared from 60 mg. of *p*-toluidine was added drop by drop while the solution was being cooled by ice. After the mixture had been stirred for 1.5 hr. at 0~5°C, the filtration of the reaction mixture afforded 135 mg. of red crystals (m. p. 155~160°C), the recrystallization of which from benzene gave orange needles (VI) (m. p. 187~188°C).

λ_{max}^{MeOH} mμ (log ε): 265 (4.35), 295 (4.27), 402 (4.49) and 436 (4.45).

Found: C, 80.34; H, 5.41; N, 5.79. Calcd. for $C_{25}H_{24}O_2N_2$: C, 79.97; H, 5.75; N, 6.66%.

The Formation and Hydrolysis of Methyl Ether (VII) of 3,7-Di(7-tropyl)tropolone (III). — To 5 ml. of a 2.8% ether solution of diazomethane containing a few drops of methanol, 100 mg. of III were added and the mixture was allowed to stand overnight at room temperature. The removal of the ether afforded 70 mg. of crystals (m. p. 80~82°C), which on recrystallization from methanol gave yellowish crystals (VII) (m. p. 85~86°C). IR (Nujol): no OH group, 1590, 1560 (C=O and C=C), 745, 704 cm^{-1} (tropyl group).

λ_{max}^{MeOH} mμ (log ε): 322 (3.80).

Found: C, 83.51; H, 5.79. Calcd. for $C_{22}H_{20}O_2$: C, 83.51; H, 6.37%.

The solution of 7 mg. of VII dissolved in 1 ml. of ethanol containing five drops of 6 N hydrochloric acid was refluxed for 30 min. After the removal of the ethanol and dilution with water, the reaction mixture was extracted with benzene. Evaporation of benzene extract, after it had been dried on sodium sulfate, afforded 5 mg. of crystals (m. p. 130°C), which were found to be identical with III by a comparison of their infrared spectra.

The Catalytic Hydrogenation of 3,7-Di(7-tropyl)-tropolone (III). — A solution of 38 mg. of III dissolved in 2 ml. of ethanol was catalytically reduced in the presence of 10 mg. of platinum oxide at an ordinary temperature and pressure. 26 ml. of hydrogen (9 molar equivalent) were absorbed over a 70 min. period. After the removal of the catalyst by filtration, evaporation of the ethanol afforded 32 mg. of colorless crystals (m. p. 52~55°C), the recrystallization of which from ethanol gave colorless needles (VIII) (m. p. 59~60°C). IR (oily state): 3500 (OH), 2900, 2850 (CH) 1700 cm^{-1} (C=O).

Found: C, 78.77; H, 10.87. Calcd. for $C_{21}H_{36}O_2$: C, 78.69; H, 11.32%.

The Separation of Isomeric Compounds (IX and X) from the Reaction of Tropylium Bromide and Tropolone. — The reaction of 13.6 g. of tropylium bromide and 10.0 g. of tropolone was carried out in as the way described above. The oily product thus obtained was distillated under reduced pressure to give three fractions as follows. (1) 3.94 g. of an oil (b. p. 90°C/3 mmHg) which crystallized to colorless crystals (m. p. 40°C). Recrystallization from benzene gave crystals, melting at 47°C, which were identified as recovered tropolone by a comparison of their infrared spectra. (2) 1.21 g. of an oil (b. p. ~190°C/3 mmHg). (3) 2.41 g. of an oil (b. p. 190~192°C/3 mmHg). Fractions 2 and 3 were found to be almost the same by a comparison of their infrared spectra and by paper chromatography which showed the existence of two major components. The sodium salt obtained from 2 g. of fraction 3 was fractionally recrystallized from a water-ethanol mixture to give the following fractions. From the most sparing fraction, 635 mg. of the salt was obtained, which on acidification with 2 N hydrochloric acid it gave 350 mg. of crystals (m. p. 65~67°C). Recrystallization from petroleum ether afforded yellow needles (IX) (m. p. 97~98°C). IR (KBr): 3180 (OH), 1602, 1550 (C=O, C=C), 750, 732 cm^{-1}.

Found: C, 79.03; H, 5.64. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

The acidification of 1.02 g. of the second fraction of the salt afforded 750 mg. of crystals (m. p. 40~50°C), which on recrystallization from ethanol gave yellow needles (X) (m. p. 59~60°C). IR (KBr): 3235 (OH), 1600, 1594, 1545 (C=O, C=C) 725, 704 cm^{-1}.

Found: C, 78.04; H, 5.36. Calcd. for $C_{14}H_{12}O_2$: C, 79.22; H, 5.70%.

The oil, obtained from 300 mg. of the most easily soluble salt by acidifying it with acid, could not be identified because of its lability.

The Coupling of 3-Tropyltropolone (X) with *p*-Toluenediazonium Chloride.—To a solution of 160

mg. of X dissolved in 1 ml. of pyridine, *p*-toluenediazonium chloride prepared from 97 mg. of *p*-toluidine was added drop by drop while the solution was being cooled by ice. After it has been stirred and ice-cooled for 2 hr. and had been diluted with water, the reaction mixture was extracted with chloroform. The extract was washed with water, dried on sodium sulfate and evaporated to give 120 mg. of red crystals (m. p. 120~125°C), the recrystallization of which from a benzene-ethanol mixture afforded yellow needles (XI) (m. p. 148~149°C).

λ_{max}^{MeOH} mμ (log ε): 233 (4.22), 307 (4.13), 400 (4.53) and 440 (sh).

Found: C, 76.91; H, 5.43; N, 7.82. Calcd. for $C_{21}H_{18}O_2N_2$: C, 76.34; H, 5.49; N, 8.43%.

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