

Reactions of Alkyltropylium Ions with a Base¹⁾Tetsuo NOZOE,²⁾ Kazuko TAKAHASHI and Hiroshi YAMAMOTO³⁾*Department of Chemistry, Faculty of Science, Tohoku University, Katahira-cho Sendai*

(Received May 13, 1969)

On the reaction with a base (*e.g.*, aqueous sodium hydroxide), isopropyl- and methyl-tropylium ions afforded cycloheptatrienyl polymers with an alkylene bridge, such as IIIa and IIIb, while the *t*-butyltropylium ion gave a mixture of 3- and 4-*t*-butyltropone, which was then transformed to 4- and 5-*t*-butyltropone (VIIIa and IX). The bromination of VIIIa with 3 mol of bromine in methanol gave 3,7-dibromo-4-*t*-butyl-2-methoxy-2,3-dihydrotropone (XIIa). On the heating of the adduct (XIIa) at 130°C, 7-bromo-4-*t*-butyltropone (XIa) was formed.

It has been reported that the tropylium ion reacts with phenols,⁴⁾ aromatic amines,⁵⁾ and arylmagnesium halides⁶⁾ to give arylcyclohep-

tatrienes, the dehydrogenation products of which, aryltropylium ions, are very stable in an aqueous solution or in the solid state. Upon the treatment of aryl-(such as phenyl- or *p*-methoxyphenyl)-tropylium ions with alkali, followed by the disproportionation reaction,^{7,8)} aryltropones have been

1) Partially presented at the 17th Annual Meeting of the Chemical Society of Japan, Tokyo, March, 1964.

2) Present address: No. 811, 2-5-1, Kamiyoga, Setagaya-ku, Tokyo.

3) Present address: Department of Chemistry, Faculty of Science, Okayama University, Okayama.

4) a) T. Nozoe and K. Kitahara, *Chem. & Ind.*, **1962**, 1192; b) R. van Helden, A. P. ter Borg and A. F. Bickel, *Rec. Trav. Chim.*, **81**, 599 (1962); c) P. Bladon, P. L. Pauson, G. R. Proctor and W. J. Rodger, *J. Chem. Soc.* **1966**, (C), 926; d) K. Takahashi, *This Bulletin*, **40**, 1462 (1967); e) J. J. Looker, *J. Org. Chem.*, **32**, 2941 (1967).

5) a) J. J. Looker, *J. Org. Chem.*, **30**, 4180 (1965); b) T. Nozoe, K. Kitahara and H. Susumago, to be published; c) T. Nozoe, K. Takahashi and H. Susumago, to be published.

6) C. Yutz and F. Voithenleitner, *Chem. Ber.*, **97**, 29 (1964).

7) T. Ikemi, T. Nozoe and H. Sugiyama, *Chem. & Ind.* **1960**, 932.

8) A. P. ter Borg, R. van Helden, A. F. Bickel, W. Renold and A. S. Dreiding, *Helv. Chim. Acta*, **43**, 457 (1960).

TABLE 1. NMR SPECTRA

Compounds	τ -Values† for protons ^{a)}							Substituents	
	H (7)	H (1)	H (2)	H (3)	H (4)	H (5)	H (6)		
<i>Cycloheptatrienes</i>									
Ia	8.84 m	4.85 dd <i>J</i> 9.5, 6.0	3.89 m	3.44 m	3.44 m	3.89 m	4.85 dd	8.99 d, <i>J</i> 6.0	8.23 dsep <i>J</i> 8.5, 6.0
Ib	8.5 m	4.49 dd <i>J</i> 8.5, 5.0	3.93 m	3.42 m	3.42 m	3.93 m	4.49 dd	8.69 dbr <i>J</i> 6.0	
Ic	8.87 t <i>J</i> 6.0	4.77 dd <i>J</i> 9.5, 6.0	3.88 m	3.41 tm <i>J</i> 3, 0.7	3.41 tm	3.88 m	4.77 dd	8.97 s	
3 ^{b)} -(VIa)	7.85 t <i>J</i> 6.8	4.78 dt <i>J</i> 9.0, 6.8	3.90 d <i>J</i> 9.0	—	3.66 d <i>J</i> 6.0	3.94 dd <i>J</i> 9.0, 6.0	4.78 dt <i>J</i> 9.0, 6.8	8.88 d, <i>J</i> 6.5	7.2—8.0 m
3-(VIb)	7.82 t <i>J</i> 6.8	4.75 dt <i>J</i> 9.0, 6.8	4.10 d <i>J</i> 9.0	—	3.68 d <i>J</i> 6.0	4.00 dd <i>J</i> 9.0, 6.0	4.79 dt <i>J</i> 9.0, 6.8	7.97 s	
3-(VIc)	7.88 t <i>J</i> 6.8	*	—	—	—	—	—	8.82 s	
1-(VIa)	7.79 d <i>J</i> 6.6	—	—	—	—	—	—	8.92 d, <i>J</i> 6.5	7.3—8.2 m
1-(VIb)	7.77 d <i>J</i> 6.8	—	4.17 d <i>J</i> 3.0	3.69 tt <i>J</i> 3.0, 0.7	3.69 tt	4.07 dd <i>J</i> 9.0, 0.7	4.80 dt <i>J</i> 9.0, 6.8	8.06 sbr	
1-(VIc)	7.78 d <i>J</i> 6.8	—	—	—	—	—	—	8.87 s	
2-(VIc)	7.91 t <i>J</i> 6.8	—	—	—	—	—	—	8.90 s	

Compounds	τ -Values† for protons ^{a)}						Substituents	
	OH (2)	H (3)	H (4)	H (5)	H (6)	H (7)		
<i>Tropolones</i>								
VIIIa	0.90 s	2.61 d <i>J</i> 1.5	—	2.90 m	2.90 m	2.90	8.65 s	
IX	1.67	2.47 <i>J</i> 11.0	2.66 <i>J</i> 11.0, 1.2	—	2.66 <i>J</i> 11.0, 1.2	2.47 <i>J</i> 11.0	8.67 s	
XIa	0.99 s	2.55 d <i>J</i> 2.0	—	3.14 dd <i>J</i> 11.0, 2.0	2.00 d <i>J</i> 11.0	—	8.63 s	
XIIa	4.94 m	5.30 d <i>J</i> 1.7	—	4.15 dd <i>J</i> 9.5, 1.7	2.65 d <i>J</i> 9.5	—	8.77 s (<i>t</i> -Bu) 6.96 s (OMe)	
XIIb	4.91 m	5.27 d <i>J</i> 1.7	—	4.12 dd <i>J</i> 9.0, 1.7	2.62 d <i>J</i> 9.0	—	8.76 s (<i>t</i> -Bu) 8.96 t, 6.75 q (OEt) <i>J</i> 6.0	

Compounds	ppm-Values for protons ^{a)}				substituents	
	seven-membered ring					
<i>Alkyl cycloheptatrienium ions</i>						
IIb			9.10			3.24 s
IIa			9.24			3.73 m, 1.60 d <i>J</i> 6.8
IIc			9.33			1.71 s

a) In carbon tetrachloride as solvent, except for IX (deuteriochloroform).

b) The initial number denotes the position of the substituent on the cycloheptatriene ring.

c) In trifluoroacetic acid as solvent.

† br, Broad; s, singlet; d, doublet; dd, double doublet; t, triplet; dt, double triplet; sep, septet; m, multiplet; *J* in Hz.

* The spectrum is too complicated to determine the chemical shift remained blank.

obtained. Tropylium ions carrying alkyl side chains have also been studied to some extent.^{9,10)}

9) H. J. Dauben, F. A. Gadecki, K. M. Harmon and D. L. Pearson, *J. Am. Chem. Soc.*, **79**, 4557 (1957).

10) D. N. Kursanov and M. E. Vol'pin, *Doklady Akad. Nauk S.S.S.R.*, **113**, 339 (1957).

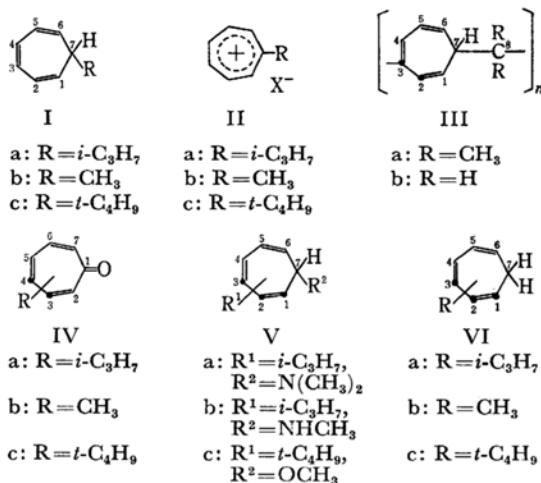
However, a more detailed investigation of alkyl-tropylium ions would be desirable, because the ions could be precursors of alkyltropolones and alkyltropolones,^{7,8,11)} which mostly cannot be prepared

11) M. E. Vol'pin, Z. N. Parnes and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, **1960**, 950.

by the direct alkylation of tropone or tropolone. In view of these points, our intense interest was focused on the reaction of alkyltropylium ions with the base.

7-Isopropylcycloheptatriene¹²⁾ (Ia), prepared in a good yield by the reaction of ethoxycycloheptatriene with isopropylmagnesium bromide, was kept at 175°C for 1.5 hr in order to cause a thermal isomerization of the double bonds.¹³⁻¹⁵⁾ The intramolecular 1—5 H shift of Ia gave an isomeric mixture of 3-, 1- and 7-isopropylcycloheptatriene in the ratio of 6:3:1. The positions of the isopropyl group and the ratio of the products were determined on the basis of the NMR spectral data (cf. Table 1). The mixture was treated with phosphorus pentachloride to afford the isopropyltropylium ion (IIa) ($X = \frac{1}{2}PtCl_6$). The spectral data of IIa, recorded in the Experimental section, were consistent with the structure. Although the cation (IIa) was very stable in an acidic medium, it changed to a colorless amorphous powder on treatment with a base such as aqueous sodium hydroxide or sodium bicarbonate, and no isopropyltropylium alcohol or isopropyltropone (IVa) was detected. The powder contained virtually no oxygen atoms (on the evidence of elemental analysis), and the infrared (IR) spectrum showed no hydroxy, carbonyl, or ether bands. The NMR spectrum (in CCl_4) had three, very broad signals at τ 3.55, 4.15, and 4.90 typical of a cycloheptatrienyl system and two broad signals at 8.5 and 8.8. The ratio of the intensities of the down- and the up-field signals was approximately 5:7. These spectral data, together with the unusual broadness of the signals and the possible modes of formation of the compound (see below), suggested that it was a polymer and that it most likely had the structure IIIa.

When 7-methylcycloheptatriene⁹⁾ (Ib) was heated at 170°C for 3.5 hr, a mixture of 3- and 1-methylcycloheptatriene was obtained in the ratio of 1:2 (from the NMR spectrum). The treatment of the mixture with phosphorus pentachloride gave the methyltropylium ion⁹⁾ (IIb) ($X = \frac{1}{2}PtCl_6$), which was very stable in the solid state and in a strongly acidic aqueous solution. However, a weakly acidic (pH 3—5) or neutral solution of IIb gradually turned orange and finally yielded a colorless, amorphous powder. The formation of the material was also demonstrated, but in a better yield, when an aqueous solution of IIb was treated with sodium



hydroxide, but the reaction was accompanied by the formation of a trace (1%) of methyltropone¹⁶⁾ (IVb) as the by-product (ν_{max} 1630, 1590 cm^{-1}). The main product was shown by the IR spectrum to possess methine, methylene, and cycloheptatriene groups, but no hydroxy nor carbonyl group, although all bands were very broad (cf. Experimental section). The spectral evidence presumably verifies the structure IIIb for the compound.

The formation of the polymers IIIa and IIIb could reasonably be explained in terms of the attack of a hydroxide anion on the α -hydrogen atom, H_A, in the formula A, rather than on the seven-membered ring; thus, the heptafulvene-type compound B could be formed as an intermediate. It is at present uncertain on which site of the cycloheptatriene ring the polymerization reaction takes place, but the products are considered to be a mixture of the alkylated cycloheptatriene polymers with an alkylene bridge at the 3,7 and 2,7 positions, assuming that the negatively-charged carbon (C-8) in the formula B, instead of a hydroxide anion,¹⁷⁾ attacks the 4- or 3-position of the seven-membered ring of another molecule (a steric repulsion would prevent the 2—8 polymerization). The fact that the methyltropylium ion (IIb) required a stronger acidic medium than IIa to keep the cation stable indicated that the stability of the two alkyltropylium ions, IIa and IIb, depend on the acidity of the medium. A similar phenomenon had been observed in aliphatic alkenyl cation systems.¹⁸⁾

12) W. von E. Doering and L. H. Knox, *J. Am. Chem. Soc.*, **75**, 297 (1953).

13) A. P. ter Borg, H. Kloosterziel and N. van Meurs, *Rec. Trav. Chim.*, **82**, 717 (1963); A. P. ter Borg and K. Kloosterziel, *ibid.*, **82**, 741 (1963).

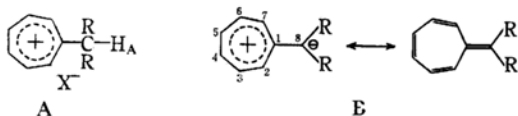
14) K. W. Egger, *J. Am. Chem. Soc.*, **89**, 3688 (1967).

15) T. Nozoe and K. Takahashi, *This Bulletin*, **38**, 665 (1965).

16) The position of the methyl group is uncertain. The product would be a mixture of 4-, 3- and 2-methyltropone.

17) It has been reported that a hydroxy anion attacks the 3- or 4-position of aryltropylium ions, giving 3- or 4-aryltropones. See Refs. 4 and 7.

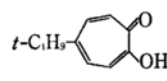
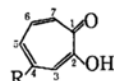
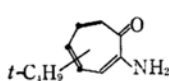
18) N. C. Deno, H. G. Rickey, Jr., N. Friedman, J. D. Hodge, J. J. Houser and C. U. Pittman, Jr., *J. Am. Chem. Soc.*, **85**, 2991 (1963).



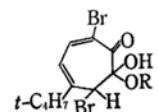
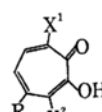
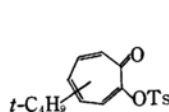
When the isopropyltropylum ion (IIa) was allowed to react with dimethylamine, a mixture of 1-, 2- and 3-isopropyl-7-dimethylaminocycloheptatriene (Va) was formed. By the same reaction with monomethylamine, a mixture of 1-, 2-, and 3-isopropyl-7-methylaminocycloheptatriene (Vb) was obtained. Although the methyltropylum ion (IIb) gave no clear substance, it was noteworthy that, upon treatment with alkylamines, the cation IIa did not undergo a polymerization reaction but instead afforded the *N*-alkylaminocycloheptatriene derivatives. A similar treatment of IIa with methanolic sodium bicarbonate, however, mostly afforded the polymer IIIa.

These observations led us to a further study of the *t*-butylcycloheptatrienium ion (IIc) which has no acidic hydrogen atom at the α -position of the substituent. Upon the heating of 7-*t*-butylcycloheptatriene (Ic), prepared in a good yield by the reaction of 7-ethoxycycloheptatriene with *t*-butyl magnesium chloride, at 175°C for 2 hr, a mixture of 7-, 3-, 1- and 2-*t*-butylcycloheptatriene was obtained in the ratio of 1 : 2.2 : 10 : 2 (from NMR). The subsequent dehydrogenation of the mixture with phosphorus pentachloride in carbon tetrachloride gave the stable cation, IIc ($X = \frac{1}{2}PtCl_6$). A considerable amount of 7- and 1-*t*-butylcycloheptatriene was recovered unchanged in the above reaction, indicating that the hydride abstraction from the sterically-hindered 7-position of the cycloheptatriene seemed to be relatively difficult. The treatment of the cation IIc with sodium hydroxide afforded an oily stuff, di-(*t*-butylcycloheptatrienyl) ether, which was then converted with a trace of acid into the tropone (IVc) and the cycloheptatriene (VIc). The IR band of IVc observed at 1623 cm^{-1} was attributed to the carbonyl group. A broad peak due to the ring protons appeared at τ 3.1 in the NMR spectrum (in CCl_4). Although IVc showed a sharp singlet due to the *t*-butyl group at τ 8.72 and gave one 2,4-dinitrophenylhydrazone, mp 182–184°C it was assumed to be a mixture of 3- and 4-*t*-butyltropone, because two spots (R_f 0.7, 0.6) appeared on an alumina thin-layer plate in a ratio of *ca.* 2 : 1 (benzene-ethyl acetate, 20 : 1, as the solvent). The moiety, VIc, was concluded to be a nearly equivalent amount of a mixture of 1-, 2-, and 3-*t*-butylcycloheptatriene, considering the presence of three methylene signals at τ 7.78 (d), 7.88 (t), and 7.91 (t), and three singlets of approximately the same intensities due to *t*-butyl groups at 8.83, 8.87, and 8.90 in the NMR spectrum (in CCl_4). The treatment of a methanolic solution of IIc with sodium bicarbonate gave a 1 : 1 mixture of 2- and 3-*t*-

butyl-7-methoxycycloheptatriene (Vc), the structures of which were derived from the NMR spectrum (see Experimental section). No polymerized hydrocarbon similar to IIIa and IIIb was produced on the treatment of the cation IIc with the base.



a: $R = t-C_4H_9$
b: $R = i-C_3H_7$



a: $R = t-C_4H_9$,
 $X^1 = Br$, $X^2 = H$
b: $R = i-C_3H_7$,
 $X^1 = X^2 = Br$

[c: $R = t-C_4H_9$, $X^1 = X^2 = Br$]

The two *t*-butyltropolones, VIIIA and IX, were successfully synthesized by treating the tropone (IVc) with hydrazine hydrate, followed by the hydrolysis of the resulting aminotropone mixture (VII) with alcoholic potassium hydroxide. The tropolone (VIIIA) readily gave the sodium salt as yellow crystals with aqueous sodium carbonate, while the tropolone (IX) formed hardly any salt under the same conditions. Thus, IX could be extracted from the above basic layer with chloroform or ether; the separation and purification of VIIIA and IX from the crude mixture were effectively achieved by repetition of the above procedure. The yields of VIIIA and IX from the tropone mixture (IVc) were 40 and 1% respectively. The IR spectrum of VIIIA showed absorption bands at 3226 and 1610 cm^{-1} typical of the hydroxy and carbonyl group of tropolones. The ring protons of VIIIA appeared in the NMR spectrum as a doublet (1H) at τ 2.61 ($J = 1.5$ Hz) and as a multiplet (3H) at 2.90, as may be expected for 4-substituted tropolone systems. The assignment of the signals is shown in the table. The structure was confirmed by the degradation of the tosyl ether (X) to 3-*t*-butylbenzoic acid on refluxing in alcoholic potassium hydroxide.

The minor product mentioned above was proved to be 5-*t*-butyltropolone¹⁹⁾ (IX), by taking account of the A_2B_2 -octet signal centered at τ 2.57 ($J_{ab} = J_{a'b'} = 11.0$, $J_{aa'} = 1.2$, $J_{bb'} \approx 0$ Hz) in the NMR spectrum (*cf.* the table). The hydroxyl and

19) T. Nozoe, H. Kishi and A. Yoshikoshi, *Proc. Japan Acad.*, **27**, 149 (1951).

carbonyl absorption bands appeared at 3247 and 1616 cm^{-1} respectively. The ultraviolet spectra of both VIIIa and IX are recorded in the Experimental section. When phenyl- and *p*-methoxyphenyl-tropolone were synthesized from the corresponding aryltropylium ions by the procedure described above, the relative ratio of 4- and 5-aryl-substituted tropolone was about 3:1.^{4d,7)} The present study, however, showed that the 4-substituted tropolone (VIIIa) was produced in a much larger amount than the 5-substituted compound (IX); the reason for this we have not yet made clear. Nevertheless, this procedure would seem to be a useful approach for the synthesis of 4-*t*-butyl-tropolone.

In order to examine the steric influence of the bulkier alkyl group of VIIIa, the bromination of VIIIa and 4-isopropyltropolone (VIIIb)²⁰⁾ was carried out in order to compare their reactivities. When one mole of bromine in methanol was used, VIIIa was shown to give 7-bromo-4-*t*-butyltropolone (XIa) on the evidence of the elemental analysis and the spectral data (cf. table and the Experimental section). The treatment of VIIIa with 3 mol of bromine in the same solvent, however, afforded a non-aromatic addition product (XIIa) the structure of which was derived from the IR (3367, 1667 cm^{-1} : non-tropolone ring) and the NMR (see table) spectra. On refluxing in ethanol, the methoxy group of XIIa was replaced by an ethoxy group, giving the adduct (XIIb). On the other hand, VIIIb mainly afforded the dibromo derivative²¹⁾ (XIb) on the bromination of 3 mol in methanol.

The possibility of the removal of methanol from the adduct (XIIa) to yield a dibromotropolone (XIc) similar to XIb was then examined. Although XIIa mostly remained unchanged at 80°C/1 mmHg (3 hr), it was unexpectedly converted to the monobromotropolone (XIa) upon heating at 130°C for 20 min. This suggested that a large steric repulsion between the *t*-butyl group and the bromine atom on C-3 of the compound XIIa prevented the formation of the more sterically hindered dibromotropolone (XIc) but, upon heating, facilitated the removal of the bromine atom to give XIa. The steric effect of a *t*-butyl group in seven-membered aromatics appeared to be remarkable; it is now being examined in detail.

Experimental

Materials for the analyses were dried over P_2O_5 at about 20°C/20 mmHg overnight. The NMR spectra

20) Recent study on bromination and chlorination of halotropones and 2-methoxytropone was carried out by T. Nozoe, K. Takase and M. Yasunami: See Ph. D. thesis of M. Yasunami, Tohoku University (1965).

21) T. Nozoe, T. Mukai and K. Takase, *Proc. Japan Acad.*, **26**, 19 (1950).

were obtained with a Varian A-60 spectrometer, operating at 25°C and 60 Mc/sec, with tetramethylsilane (τ 10) as the internal standard.

7-Isopropylcycloheptatriene (Ia). A mixture of 68.9 g of isopropyl bromide and 200 ml of dry ether was slowly stirred into 13.6 g (1 equiv.) of magnesium over a 2.5 hr period at such a rate that the mixture was gently refluxed; then it was stirred for a further 30 min. A solution of 61.1 g (0.8 equiv.) of 7-ethoxycycloheptatriene¹⁵⁾ in 100 ml of dry ether was stirred in over a 1.5 hr period and then stirring was continued for another hour. Into the mixture cooled with an ice bath there was stirred, 500 ml of cold 2N hydrochloric acid over a 30 min period. The reaction mixture was extracted with ether, and the ether was washed with cold water and dried over MgSO_4 . After the solvent had been evaporated, the residue was distilled to give 48.1 g (80%) of a colorless oil, Ia; bp 82–86°C/42 mmHg. The specimen for the analysis was distilled at 74°C/33 mmHg.

Found: C, 89.72; H, 10.46%. Calcd for $\text{C}_{10}\text{H}_{14}$: C, 89.49; H, 10.51%. $\nu_{\text{max}}^{\text{neat}}$ 2967, 2919, 2833, 1445, 1385, 1368, 1193, 1164, 950, 799, 743, 704 and 685 cm^{-1} .

7-Methylcycloheptatriene (Ib). This was obtained from methylmagnesium iodide and 7-ethoxycycloheptatriene by the above procedure in a 71% yield (bp 63°C/80 mmHg).

7-*t*-Butylcycloheptatriene (Ic). This was similarly made from *t*-butylmagnesium chloride and 7-ethoxycycloheptatriene as a colorless oil. (55% yield); bp 95–98°C/45 mmHg.

Found: C, 89.37; H, 10.83%. Calcd for $\text{C}_{11}\text{H}_{16}$: C, 89.12; H, 10.88%. $\nu_{\text{max}}^{\text{neat}}$ 2994, 2941, 2857, 1464, 1389, 1366, 1250, 1208, 1190, 1011, 952, 852, 741 and 703 cm^{-1} .

Thermal Isomerization of the Cycloheptatrienes (Ia, b, c). The substance was heated in a sealed tube at a given temperature ($\pm 0.5^\circ\text{C}$), and then purified by distillation. When 12 g of Ia were heated at 175°C for 1.5 hr, and then distilled, 11 g of a mixture consisting of 3-, 1-, and 7-isopropylcycloheptatriene (6:3:1) was obtained as a colorless oil; bp 78–79°C/37 mmHg.

Found: C, 89.79; H, 10.43%. Calcd for $\text{C}_{10}\text{H}_{14}$: see above.

The heating of 18.3 g of Ic at 175°C for 2 hr, followed by distillation, gave 17.5 g of a mixture of 7-, 3-, 1-, and 2-*t*-butylcycloheptatriene (1:2.2:10:2) as a colorless oil; bp 88–89°C/37 mmHg.

Found: C, 89.40; H, 10.69%. Calcd for $\text{C}_{11}\text{H}_{16}$: see above.

Isopropyltropylium Ion (IIa). Into a suspension of 3.3 g of phosphorus pentachloride (2.1 equiv.) in 25 ml of anhydrous carbon tetrachloride there was stirred a solution of 1.00 g of the above thermally-isomerized isopropylcycloheptatriene mixture in 5 ml of carbon tetrachloride. After the mixture had been stirred for 7 hr and then set aside overnight at room temperature, the precipitate was filtered off in a dry box, dried over P_2O_5 *in vacuo*, and poured into 1 ml of cold acetonitrile. To the solution, after clarification by filtration, there was added, drop by drop, a saturated solution of $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in acetonitrile, giving 1.00 g (40%) of IIa (as the hexachloroplatinate) as yellow prisms; mp 164°C (decomp.).

Found: C, 35.93; H, 3.94; Pt, 29.55%. Calcd for $\text{C}_{10}\text{H}_{13} \cdot 1/2\text{PtCl}_6$: C, 35.63; H, 3.89; Pt, 28.94%. $\lambda_{\text{max}}^{\text{MeCN}}$

271, 362 sh μm . $\nu_{\text{max}}^{\text{KBr}}$ 2941, 2899, 1527, 1481, 1464, 1449, 1395, 1284, 1235, 1058, 1021, 945, 887, 879, 862 and 754 cm^{-1} . $\delta_{\text{CF}_3\text{CO}_2\text{H}}$ 1.59 (d, $J=6.8$ Hz; 2Me), 3.89 (q, $J=6.8$ Hz; CH), 9.59 (s; 6H).

Methyltropylium Ion (IIb). This was obtained by the same procedure as above in a 37% yield as a brownish yellow crystalline powder; mp 160°C (blackened).

Found: C, 32.58; H, 3.23; Pt, 32.57%. $\nu_{\text{max}}^{\text{KBr}}$ 3012, 1522, 1486, 1449, 1359, 1282, 1235, 1164, 1027, 979, 965, 867 and 727 cm^{-1} . $\delta_{\text{CF}_3\text{CO}_2\text{H}}$ 3.31 (s; Me), 9.08 (s; 6H).

***t*-Butyltropylium Ion (IIc).** This was similarly prepared. The hexachloroplatinate isolated in a 38% yield was in the form of pale orange needles; mp 181°C (decomp.).

Found: C, 37.32; H, 4.28; Pt, 27.67%. Calcd for $\text{C}_{11}\text{H}_{15}\cdot 1/2\text{PtCl}_6$: C, 37.63; H, 4.31; Pt, 27.78%. $\lambda_{\text{max}}^{\text{MeCN}}$ 272, 346 sh μm . $\nu_{\text{max}}^{\text{KBr}}$ 2976, 2933, 1595, 1570, 1522, 1490, 1439, 1385, 1292, 1067, 1056, 947, 820, and 770 cm^{-1} .

The Reaction of IIa with Sodium Bicarbonate. Five grams of the thermally-isomerized isopropylcycloheptatriene was treated with 16.1 g (2.1 equiv.) of phosphorus pentachloride in 110 ml of carbon tetrachloride according to the above procedure. After 7 hrs' stirring at room temperature, 50 ml of ice water was stirred into the cooled mixture. After 10 mins' stirring at 0°C, the contents were separated and the aqueous layer was quickly washed with 10 ml of cold chloroform. Solid sodium bicarbonate enough to give pH 5–6 was stirred into the cooled aqueous layer, and then the mixture was stirred for 30 min, and then basified by the addition of further sodium bicarbonate (pH 8). The contents turned orange during this basification. The sodium chloride precipitated was filtered off and washed with chloroform. The filtrate was extracted with chloroform, and the combined extract was dried over anhydrous K_2CO_3 . The evaporation of the solvent below 25°C (bath) under reduced pressure left 3.23 g of a viscous orange oil, which gradually solidified on being set aside at room temperature. The material dissolved in benzene reprecipitated in methanol for purification (three times), giving IIIa as a white amorphous solid (65% yield); mp 150–154°C.

Found: C, 88.05; H, 8.59%. $\nu_{\text{max}}^{\text{KBr}}$ 2985, 2924, 2833, 2577, 1456, 1376, 1357, 1214 w, 1183 w, 830, 794 and 727 cm^{-1} . The basification of the aqueous solution of IIa with cold 5N sodium hydroxide produced the same polymer.

The Reaction of IIb with Sodium Hydroxide.

An aqueous solution of IIb, prepared from 3.5 g of the above isomerized methylcycloheptatriene and 15.1 g of phosphorus pentachloride, was alkalinized with 8N sodium hydroxide (pH 9) and subjected to the same treatment as above; this gave a viscous orange liquid. Two purifications of the oil by reprecipitation from benzene-methanol gave IIb as a pale yellow amorphous solid (57% yield); mp above 260°C. $\nu_{\text{max}}^{\text{KBr}}$ 3030, 2924, 2857, 1439, 1389, 763, 730 and 712 cm^{-1} (All the bands were very broad.).

The combined filtrate of the above purification was evaporated, and the residue, dissolved in benzene, was passed through an alumina column. The evaporation of the benzene-elute under reduced pressure gave 30 mg of a yellow oil which was assumed, from its IR spectrum (1630 and 1590 cm^{-1}), to be a mixture of the methyl-

tropones (IVb) (1% yield). The oil was refluxed with 40 mg of 2,4-dinitrophenylhydrazine in 20 ml of ethanol (with a trace of hydrochloric acid) for 10 min. The precipitate was then collected and recrystallized from benzene, giving 30 mg of reddish-brown plates; this substance was considered to be the 2,4-dinitrophenylhydrazone of IVb, mp 230–232°C.

Found: C, 56.93; H, 3.98; N, 18.06%. Calcd for $\text{C}_{14}\text{H}_{12}\text{N}_4\text{O}_4$: C, 56.00; H, 4.03; N, 18.66%.

The Reactions of IIa with Alkylamines (Va and Vb).

a) An aqueous solution of IIa, prepared from 20 g of the thermally-treated isopropylcycloheptatriene and 65.3 g of phosphorus pentachloride, was added, drop by drop, into 169 g of an ice-cooled and stirred 40% aqueous solution of dimethylamine. After having been stirred for 2 hr, the mixture was extracted with ether; the extract was evaporated under reduced pressure, and then distilled, giving a mixture of 1-, 2-, and 3-substituted Va as a yellow oil (72% yield); bp 66–67°C/1.3 mmHg.

Found: C, 81.60; H, 10.89; N, 8.23%. Calcd for $\text{C}_{11}\text{H}_{19}\text{N}$: C, 81.30; H, 10.80; N, 7.90%. $\nu_{\text{max}}^{\text{NaCl}}$ 2959, 2865, 2829, 2786, 1464, 1458, 1385, 1366, 1304, 1277, 1217, 1174, 1153, 1103, 1064, 1042, 1013, 1001, 911, 898, 878, 867, 839, 798, 768, 755 and 731 cm^{-1} . τ_{CCl_4} 8.97 (d, J 6.6 Hz; *i*-Pr), 8.89 (d, J 6.6 Hz; *i*-Pr), 8.86 (d, J 6.6 Hz; *i*-Pr), 8.22 (m; J 6.6 Hz; H-7), 7.74 (s; NMe_2), 7.45 (m; *i*-Pr-methine), 4.80, 4.02, 3.51 (m; ring protons).

b) The similar treatment of IIa with an excess 30% aqueous solution of methylamine gave Vb as a yellow oil (35% yield); bp 70–71°C/3 mmHg.

Found: C, 80.68; H, 10.27; N, 8.03%. Calcd for $\text{C}_{11}\text{H}_{17}\text{N}$: C, 80.92; H, 10.50; N, 8.58%. $\nu_{\text{max}}^{\text{NaCl}}$ 2950, 2857, 2778, 1456, 1445, 1377, 1359, 1311, 1290, 1181, 1136, 1100, 1028, 996, 921, 827, 800, 762 and 726 cm^{-1} . τ_{CCl_4} 8.97 (d, J 6.6 Hz; *i*-Pr), 8.90 (d, J 6.6 Hz; *i*-Pr), 8.87 (d, J 6.6 Hz; *i*-Pr), 8.3 (m; H-7), 7.62 (s, N-CH_3), 7.46 (m; *i*-Pr), 4.77, 4.08, 3.80 (m; ring protons).

The Reaction of IIc with Sodium Hydroxide: Formation of *t*-Butyltropone (IVc) and *t*-Butylcycloheptatrienes (VIc).

A solution of IIc in 100 ml of water, prepared from 7.43 g of an isomerized mixture of Ic and 20.1 g (2.1 equiv.) of phosphorus pentachloride as has been described above was slowly stirred into 60 ml of cold 33% aqueous sodium hydroxide under ice-cooling, and then the stirring was continued for 30 more min. The precipitate was then filtered off and washed with chloroform. The filtrate was extracted with chloroform, and the combined extract, washed with cold water and dried over MgSO_4 , was evaporated at 20°C/20 mmHg, affording an oily stuff. The NMR spectrum (in CCl_4) showed *t*-butyl signals as singlets at τ 8.83, 8.90, and 8.92 and an H-7 signal as a multiplet at 6.57, indicating that the oil was a mixture of di-(1-, 2- and 3-*t*-butylcycloheptatrienyl)ether. It was set aside overnight at room temperature with 0.2 ml of conc. hydrochloric acid, and then extracted with benzene after the addition of cold dilute aqueous sodium bicarbonate. The extract was washed with cold water and dried over MgSO_4 . After the evaporation of the solvent under reduced pressure, the residue was distilled, giving VIc as a colorless oil (52% yield), bp 27–29°C/0.7 mmHg, and IVc as a yellow oil (61%), bp 104–106°C/0.7 mmHg.

Found for IVc: C, 80.28; H, 8.87%. Calcd for

$C_{11}H_{14}O$: C, 81.44; H, 8.70%. ν_{\max}^{calc} 2941, 1623, 1567, 1520, 1471, 1362, 1333, 1235, 1208, 988, 902, 864, 833, 790, 740, 711 and 684 cm^{-1} . It did not give a picrate.

2,4-Dinitrophenylhydrazone of IVc. A mixture of 58 mg of IVc and 71 mg of 2,4-dinitrophenylhydrazine was refluxed for 1 hr in 2 ml of ethanol with a trace of concentrated hydrochloric acid. The precipitate was then filtered off and recrystallized from ethanol, giving dark brown needles; mp 182–184°C.

Found: C, 60.24; H, 5.03; N, 16.17%. Calcd for $C_{17}H_{16}N_4O_4$: C, 59.64; H, 5.30; N, 16.37%.

2- and 3-*t*-Butyl-7-methoxycycloheptatriene (Vc). To 150 ml of a cold aqueous solution of IIc, made by the treatment of 5.0 g of an isomerized mixture of Ic with 13.5 g of phosphorus pentachloride, there was added 15 ml of methanol, and then 40 g of sodium bicarbonate, drop by drop under ice-cooling. The contents were stirred at 0°C for a further 30 min, and then extracted with ether. The extract was washed with cold water, dried over anhydrous K_2CO_3 , and distilled, giving 1.79 g (30%) of Vc as a colorless oil, bp 64–69°C/2.5 mmHg, and 0.3 g (12%) of IVc as a yellow oil, bp 105–107°C/1.8 mmHg.

Found for Vc: C, 80.36; H, 9.46%. Calcd for $C_{12}H_{18}O$: C, 80.85; H, 10.18%. ν_{\max}^{calc} 2959, 1475, 1460, 1387, 1374, 1361, 1252, 1205, 1135, 1122, 1109, 1080, 991, 829, 799, 764, 743 and 725 cm^{-1} . τ_{C-Cl} , 8.90 (s; *t*-Bu), *1 8.83 (s; *t*-Bu), *1 6.91 (m; 2H), 6.68 (s; OMe), *2 6.67 (s; OMe), *2 4.65 (m; 4H), 4.03 (m; 3H), 3.49 (m; 3H); the two couples of the singlets (*1,2) had approximately the same intensity, showing that Vc was a 1:1 mixture of the 2- and 3-substituted cycloheptatriene.

4- and 5-*t*-Butyltropolone (VIIIa, IX). A mixture of 5.84 g of the above tropone (IVc) and 9.05 g (4 equiv.) of 80% hydrazine hydrate was refluxed in 50 ml of ethanol for 6 hr. To the residue freed from the solvent there was added 50 ml of cold water, and then the mixture was extracted with benzene. The extract was evaporated at 20°C/15 mmHg, leaving 6.24 g (86%) of the crude 2-amino-*t*-butyltropone (VII) as a reddish-brown tar (ν_{\max}^{calc} 3348, 3311, 2950, 1592, 1513, 1473, 1429, 1364, 1333, 1263, 949, 901, 792, 761 and 710 cm^{-1}). Without purification, this was dissolved in 350 ml of ethanol and 50 ml of 6N potassium hydroxide and refluxed for 10 hr. Most of the solvent was removed at below 60°C under reduced pressure; a saturated aqueous solution of sodium carbonate and ether was then added to the residue. After the mixture had been stirred for 30 min at room temperature, the precipitate, the sodium salt of 4-*t*-butyltropolone (mp > 290°C), was collected and washed with ether. The precipitate, dissolved in 25 ml of water, was brought to pH 2–3 with 2N sulfuric acid, and the freed tropolone was extracted with ether. This procedure was repeated 3–4 times until the band at 11.9 μ in the IR spectrum of the sodium salt disappeared, giving 2.5 g of the free acid (VIIIc) (in 40% overall yield from the tropone mixture) as yellowish-brown needles, mp 33–34°C, after recrystallization from light petroleum (<60°C).

Found: C, 74.34; H, 7.91%. Calcd for $C_{11}H_{14}O_2$: C, 74.13; H, 7.97%. λ_{\max}^{calc} $m\mu$ (log ϵ): 240 (4.23), 325 (3.52), 349 (3.45). ν_{\max}^{calc} 3226, 2959, 1610, 1543, 1497, 1477, 1429, 1391, 1366 w, 1348 w, 1299 sh, 1269, 1252, 1199, 943, 916, 893, 825, 756 br, 741 br and

714 br cm^{-1} . VIIIc turned green (aq. layer) and reddish brown (benzene layer) when treated with ferric chloride.

The filtrate and the ether washing obtained by the above sodium carbonate treatment were combined, and the ether was evaporated under reduced pressure. The residue, after filtration, was extracted with chloroform, and the extract (dried over Na_2SO_4) was evaporated. The residue, which crystallized on standing, was washed with a small amount of light petroleum (<60°C); the insoluble part was sublimed at 80–100°C/1 mmHg, giving IX as pale yellow prisms, mp 102–104°C.

Found: C, 74.12; H, 7.98%. Calcd for $C_{11}H_{14}O_2$: see above. λ_{\max}^{calc} $m\mu$ (log ϵ): 234.5 (4.48), 245 sh (4.40), 250 sh (4.27), 323 (4.04), 3.51 (3.87), 3.67 (3.78). ν_{\max}^{calc} 3247, 2959, 1616, 1555, 1471, 1449, 1427, 1376, 1279, 1248, 1214, 1200, 1085, 869, 856, 822, 764 and 704 cm^{-1} .

3-*t*-Butylbenzoic Acid. Into an ice-cooled solution of 0.50 g of VIIIa dissolved in 4 ml of pyridine there was slowly stirred, 0.70 g (1.3 equiv.) of *p*-toluene-sulfonyl chloride; then the mixture was stirred for 5 hr at 0°C. The mixture was poured into 15 ml of ice water and, after stirring, extracted with chloroform. The dried extract (over $MgSO_4$) was freed from the solvent, leaving a reddish-orange oil which was presumably a mixture of 4- and 6-*t*-butyl-2-tosyloxypolone (X). The oil, dissolved in 15 ml of ethanol and 15 ml of 20% aqueous potassium hydroxide, was heated under reflux for 1 hr. The ethanol was removed under reduced pressure, and the aqueous solution was brought to pH 2–3 with cold 6N sulfuric acid at 0°C. The mixture was extracted with ether; the evaporation of the dried extract (over $MgSO_4$) at 20°C *in vacuo* left a reddish liquid. The benzene solution (3 ml) of the oil was shaken with 5 ml of 10% aqueous sodium bicarbonate. The aqueous layer was brought to pH 2 with cold 6N sulfuric acid; the precipitate was recrystallized from light petroleum (<50°C), giving 0.17 g (35%) of the benzoic acid as colorless prisms, mp 132–133°C (lit.²² 127°C).

(Found: C, 74.13; H, 7.90%). ν_{\max}^{calc} 2941, 2632, 2525, 1670, 1590, 1570, 1470, 1433, 1405, 1355, 1297, 1282, 1255, 1172, 1134, 1078, 957 br, 820, 746, 720 and 695 cm^{-1} . τ_{C-Cl} , 8.62 (s; *t*-Bu), 3.61 (t, *J* 7.5 Hz; H-5), 3.39 (dt, *J* 7.2, 1.5 Hz; H-4), 3.07 (dt, *J* 7.2, 1.5 Hz; H-6), 2.87 (t, *J* 1.5 Hz; H-2), –3.00 (s; OH).

7-Bromo-4-*t*-butyltropolone (XIa). Into a solution of 0.30 g of VIIIa in 4 ml of methanol there was stirred, drop by drop at 0°C, 0.33 g (1.2 equiv.) of bromine dissolved in 1 ml of methanol. After having been stirred at 0°C for 4 hr and then set aside overnight, the mixture was evaporated under reduced pressure, leaving a yellow powder. Recrystallization from ethanol gave 0.30 g (69%) of the bromotropolone as yellow plates, mp 75–75.5°C.

Found: C, 51.90; H, 5.29%. Calcd for $C_{11}H_{13}O_2Br$: C, 51.38; H, 5.10%. λ_{\max}^{calc} $m\mu$ (log ϵ): 256 (4.30), 331 (3.48), 367 (3.48), 379 (3.50). ν_{\max}^{calc} 3226, 2933, 1603, 1575, 1538, 1466, 1441, 1387, 1362, 1351, 1289, 1214, 1190, 1109, 941, 928, 903, 848, 839, 794, 776, 746 br and 722 cm^{-1} .

3,7-Dibromo-4-*t*-butyl-2-methoxy-2,3-dihydrotropolone (XIIa). The tropolone VIIIa was treated with 3 equiv. moles of bromine under the above conditions; the recrystallization of the product from benzene-

light petroleum ($<50^{\circ}\text{C}$) gave the adduct (XIIa) as colorless needles (89%), mp $120\text{--}127^{\circ}\text{C}$ (gradually decomp.).

Found: C, 39.13; H, 4.46%. Calcd for $\text{C}_{12}\text{H}_{16}\text{O}_3\text{Br}_2$: C, 39.17; H, 4.37%. $\nu_{\text{max}}^{\text{KBr}}$ 3367, 2933, 1667, 1558, 1456, 1351, 1189, 1147, 1110, 1070, 1063, 1046, 1004, 895, 840, 825, 787 and 742 cm^{-1} .

3,7-Dibromo-4-*t*-butyl-2-ethoxy-2,3-dihydrotropolone (XIIb). A solution of 0.80 g of XIIa in 5 ml of ethanol was refluxed for 5 min; after the solvent had then been removed, the residue was recrystallized from ethanol, giving 0.60 g (73%) of the ethanol adduct (XIIb) as pale yellow needles, mp $84.5\text{--}85.5^{\circ}\text{C}$.

Found: C, 41.45; H, 4.85%. Calcd for $\text{C}_{13}\text{H}_{18}\text{O}_3\text{Br}_2$: C, 40.87; H, 4.75%. $\lambda_{\text{max}}^{\text{EtOH}}$ $m\mu$ (log ϵ): 240 (3.83), 348 (3.57). $\nu_{\text{max}}^{\text{KBr}}$ 3413, 2941, 2857, 1658, 1613, 1555, 1466, 1453, 1385, 1370, 1351, 1323, 1152, 1115, 1087, 1063, 1048, 1014, 899, 885, 851, 828, 792 and 740 cm^{-1} .

Bromination of 4-Isopropyltropolone (VIIIb) in Methanol. To an ice-cooled and stirred solution of 0.30 g of VIIIb in 5 ml of methanol there was added 0.96 g (3.0 equiv.) of bromine dissolved in 1 ml of methanol. After 2 hrs' stirring, the mixture was set aside overnight and then poured onto ice and extracted with ether. The ether extract was dried, the solvent was evaporated at room temperature, and the residue was recrystallized from methanol, affording 0.19 g of pale green needles (mp $130\text{--}133^{\circ}\text{C}$ undepressed on

admixture) identified from the IR and NMR spectra with an authentic specimen of 3,7-dibromo-4-isopropyltropolone (XIb). On the evaporation of the recrystallization filtrate, 0.12 g more of XIb (crude) was obtained from the residual fraction forming the sodium salt with saturated aqueous sodium bicarbonate. The IR spectrum of the fraction (*ca.* 0.15 g), which did not give any sodium salt with alkali, showed a hydroxy band at 3448 cm^{-1} and carbonyl bands at 1686 and 1730 cm^{-1} , suggesting the presence of an additional bromine product, but the structure had not yet been made clear.

7-Bromo-4-*t*-butyltropolone (XIa) from 3,7-Dibromo-4-*t*-butyl-2-methoxy-2,3-dihydrotropolone (XIIa). The XIIa adduct (20 mg) was heated at 130°C for 20 min under ordinary pressure. The resulting oil was then purified by sublimation at $80^{\circ}\text{C}/1.5\text{ mmHg}$, followed by sodium salt formation; this gave 11 mg of colorless crystals. The IR and NMR spectra were identical with those of XIa.

We wish to thank Professor K. Takase (of this department) for helpful discussions, Dr. C. T. Chang (National Taiwan University) for his experimental work in the isolation of 5-*t*-butyltropolone, and Mr. E. Kirii (of this department) for the preparation of the *N*-alkylamino-isopropylcycloheptatrienes.