Substituent Effects on the Acid-catalyzed Isomerization of 2-Cyclohepta-2,4,6-trienyltropone Derivatives to 2-Benzyltropones

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The acid-catalyzed isomerization of the cycloheptatriene ring of 2-cyclohepta-2,4,6-trienyltropones to give benzyltropones *via* the norcaradiene intermediate has been studied. In the cases of 7-substituted 2-cyclohepta-2,4,6-trienyltropones (**1a–f**), the first-order reaction rate is dependent on the nature of the substituent on C-7 of the tropone nucleus, and an electron-withdrawing substituent could accelerate the rearrangement. On the other hand, 2-cyclohepta-2,4,6-trienyltropones (**2a–c**), (**3a–c**), and (**4b, d**), each of which has a substituent on the cycloheptatriene ring, exhibited remarkable chemoselectivity of C–C bond cleavage of the norcaradiene intermediate. The first-order reaction rate is dependent on both the electronic nature and the position of the substituents.

Preparation of 2-cyclohepta-2,4,6-trienyltropone derivatives (**1a–f**), (**2a–c**), and (**3a–c**) is reported in the preceding paper.[1] The ^{1}H- and ^{13}C-NMR spectra of (**3a**) and (**3b**) apparently support their formulations as a rapidly equilibrating mixture of cycloheptatriene (CHT) and norcaradiene (NCD) forms even at room temperature. We have also reported previously the preparation of the substituted 2-cyclohepta-2,4,6-trienyltropone (**4b, d**) through nucleophilic reaction of substituted tricarbonyl(1,4-η-1,3,5-cycloheptatrienide)iron with 2-chlorotropone and subsequent decomplexation.[2] In compound (**4b, d**), a conformer with a quasi-axial 7-oxocyclohepta-1,3,5-trienyl (2-troponyl) group is more stable than that with quasi-equatorial 2-troponyl group, because of the non-bonded interaction of the 2-troponyl group with Ph and MeO groups.[2]

Although theoretical[3] and experimental[4,5] investigations of the CHT–NCD valence tautomerism have been carried out for some time, it is only recently that the parent norcaradiene itself has been directly observed and the kinetics of NCD–CHT tautomerization has appeared (Figure 1).[6] While the CHT form

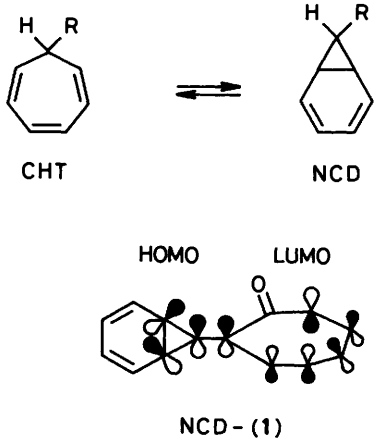


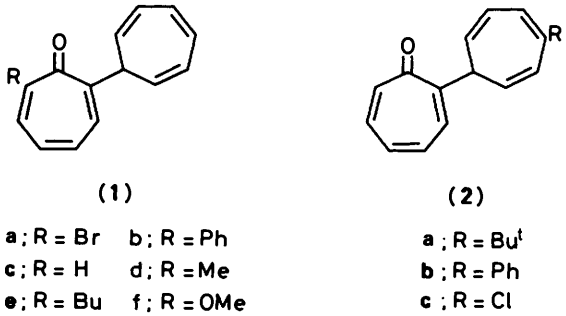
Figure 1.

is normally more stable, and the free energy difference has been revealed to be 4.0–4.5 kcal mol^{-1},[6,7] structural modification such as suitable bridging, substitution or fusion of aromatic rings can reverse the usual order of stability.[4] Regarding the 7-substituted cycloheptatrienes, the equilibrium is mainly controlled by the acceptor at C-7. According to theoretical prediction,[3] electron donation of the HOMO of the Walsh orbital of the cyclopropane ring in NCD toward the LUMO of the acceptor substituent at C-7 exhibits a tendency to shift the equilibrium to the side of the NCD form. This influence should increase along the series CN < CO_2H < CHO, and the existence of the norcaradiene tautomers for this class of compounds were confirmed experimentally.[8,9,10] Furthermore, the introduction of a cationic substituent at C-7 changes drastically the CHT–NCD equilibrium. The 7-(1,3-dioxolan-2-ylio)- and 7-(1,3-oxazolidin-2-ylio)cycloheptatriene strongly favour the norcaradiene form, and they undergo a thermal ring cleavage of the cyclopropane ring to give benzylic compounds.[11] The complexes of 7-methoxycarbonylcycloheptatriene with boron trichloride and boron tribromide also exist in the NCD form, and they rearrange thermally to methyl phenylacetate.[12] In addition, the cycloheptatriene moiety of cyclohepta-2,4,6-trienyl carbonium,[13] ethynylcyclohepta-2,4,6-trienyl carbonium,[14] and cyclohepta-2,4,6-trienyldiphenyl carbonium ions[15] also rearranges to give benzylic compounds.

In compounds (**1a–f**), (**2a–c**), (**3a–c**) and (**4b, d**), it is expected that the LUMO of the tropone[16] accepts the electron of the cyclopropane ring in NCD-(**1**) (Figure 1).[3] Moreover, protonation on the carbonyl-oxygen of tropone would lower the LUMO energy of the tropone nucleus, and increase its electron accepting character. Thus, the equilibrium of CHT–NCD would be shifted to the side of the NCD form. This paper provides full accounts for the acid-catalyzed isomerization of cycloheptatrienyltropones (**1a–f**), (**2a–c**), (**3a–c**), and (**4b, d**) to 2-benzyltropones with particular regard to CHT–NCD tautomerization and the substituent effect on reaction rate as well as on the chemoselectivity of the C–C bond cleavage in the NCD form.

Results and Discussion

Treatment of 2-cyclohepta-2,4,6-trienyltropone (**1c**) with 10 molar excess of trifluoroacetic acid (TFA) in chloroform at ambient temperature for 10 days afforded known 2-benzyltropone (**5c**)[17] in 95% yield (Scheme 1). Under similar conditions, (**1a, b**) and (**1d–f**) underwent ring cleavage to give 7-substituted 2-benzyltropones (**5a, b**) and (**5d–f**) in good yields. The reaction conditions and the yields of the products are summarized in Table 1. The structures of (**5a–f**) were assigned on the basis of their physical data including ^{13}C

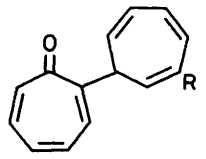


(1)

a; R = Br b; R = Ph
c; R = H d; R = Me
e; R = Bu f; R = OMe

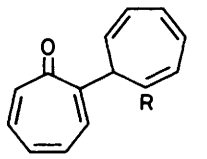
(2)

a; R = Bu^t
b; R = Ph
c; R = Cl



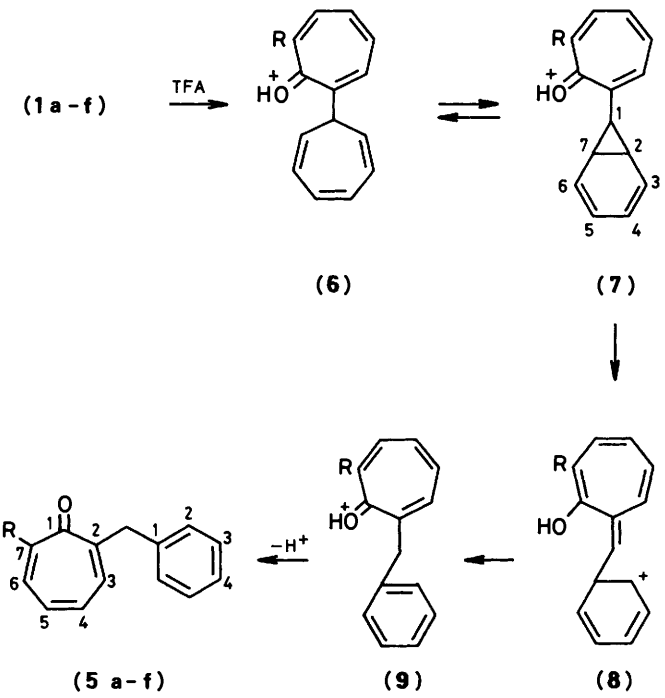
(3)

a; R = Bu^t
b; R = Ph
c; R = Cl



(4)

b; R = Ph
d; R = OMe



(1a-f) (6) (7) (5a-f) (9) (8)

a; R = Br, b; R = Ph, c; R = H, d; R = Me, e; R = Bu, f; R = OMe

Scheme 1.

NMR spectra (Table 2). Compounds (**5d–f**) are high boiling oils which darkened under distillation. Thus, satisfactory analytical data were not obtained. However, the ^{13}C (Table 2) and ^1H NMR spectra exhibited no contamination with other organic materials, and satisfactory high resolution mass spectral data were obtained. Since (**1a–f**) are very stable at ambient temperature in chloroform under neutral conditions,

Table 1. Results for the reaction of (**1a–f**) with TFA

Run	Compd.	R	Reaction time (day)	Product yield[a] (%)	k^b/s^{-1}
1	(**1a**)	Br	0.5	(**5a**) 88	1.5×10^{-5}
2	(**1b**)	Ph	1.5	(**5b**) 90	5.7×10^{-7}
3	(**1c**)	H	10	(**5c**) 95	1.7×10^{-7}
4	(**1d**)	Me	15	(**5d**) 70	1.8×10^{-8}
5	(**1e**)	Bu	15	(**5e**) 66	9.8×10^{-9}
6	(**1f**)	OMe	20	(**5f**) 51	$<5.0 \times 10^{-9}$

[a] Reactions were carried out in chloroform in the presence of 10 molar equivalent of TFA at ambient temperature. [b] The reaction rates were obtained in carbon tetrachloride at 24 °C in the presence of one molar equivalent of TFA.

TFA is indispensable for the present ring cleavage of (**1a–f**).

The reaction pathways for the isomerization of (**1a–f**) to (**5a–f**) are shown in Scheme 1. In the ^1H NMR spectra, the chemical shifts of (**1a–f**) did not exhibit appreciable change in the presence of one molar equivalent of TFA. However, protonation on the carbonyl oxygen of (**1a–f**) with TFA to give (**6**) would be the first step of the reaction sequence. The protonated tropone in (**6**) having a high π-electron accepting ability, would shift the equilibrium between (**6**) and (**7**) towards (**7**). Thus, the C(2)–C(7) bond in the three-membered ring of (**7**) would be strengthened, and both C(1)–C(2) and C(1)–C(7) bonds would be weakened.[3] Then, bond cleavage would occur in (**7**) to give the intermediate (**8**) and the subsequent proton migration would give (**9**) irreversibly.

A kinetic study of the present rearrangement was carried out in carbon tetrachloride in the presence of one molar equivalent of TFA at 24 °C. The acid concentration was assumed to be constant throughout the reaction, the plot of the logarithm of the concentrations of unchanged (**1a–f**) against the reaction time were linear. The first-order rate constants (k) thus obtained are summarized in Table 1. The reaction of (**1f**) with TFA is very slow at 24 °C, and undesirable side reactions were observed at elevated temperature (40 °C). Thus, the first order rate constant was not determined exactly, and only an estimated value is listed in Table 1 (run 6). Regarding the results summarized in Table 1, it is suggested that the tropone nucleus bearing electron-withdrawing substituents accelerate the rate of cleavage of the cycloheptatriene ring, whereas electron-donating groups, such as alkyl and methoxy, can reduce the observed rate by appreciable amounts. Thus, the observed reaction rate of the isomerization of (**1a–f**) increases along the series (**1f**) < (**1e**) < (**1d**) < (**1c**) < (**1b**) < (**1a**) (Table 1). This order parallels the electronic properties of the substituent R.[18] Regarding the rapid isomerization between CHT and NCD,[8,9] the rate determining step of the isomerization seems to be the C–C bond cleavage in (**7**).

On the other hand, the chemoselectivity of the acid-catalyzed ring cleavage of substituted cyclohepta-1,3,5-triene was also investigated by using 2-cyclohepta-2,4,6-trienyltropones (**2a–c**), (**3a–c**), and (**4b, d**) (Scheme 2). The reaction conditions and the yields of the products are summarized in Table 3. In the case of (**2a, b**), ring cleavage occurred selectively to give (**10a, b**) in good yields (runs 1 and 2). Compound (**3b**) rearranged to give (**11b**) selectively (run 4), while (**3a**) gave three products, (**10a**), (**11a**), and (**12a**) in good combined yield (run 3). The formation of (**10a**) is unexpected, and it seems to involve a skeletal rearrangement of the cycloheptatriene ring. A mixture of (**2c**) and (**3c**) in a ratio of 65:35 simply gives (**10c**) and (**11c**). Regarding the ratio of (**2c**)/(**3c**), (**10c**) and (**11c**) probably arise from (**2c**) and (**3c**), respectively (run 5). Similarly, compounds (**4b**) and (**4d**) rearranged selectively to give (**11b**) and (**11d**) (runs 6 and 7). The structures of these 2-benzyltropone

Table 2. ^{13}C Chemical shifts (ppm) of the 2-benzyltropone derivatives (**5a–f**)[a]

Compound	Tropone				Benzyl group					Remaining signals
	C-1	C-2	C-3 to C-6	C-7	CH_2	C-1	C-2	C-3	C-4	
(**5a**)	179.4	150.6	138.6, 134.9, 133.4, 129.9	141.8	41.9	138.4	129.3	128.4	126.4	—
(**5b**)	185.7	154.0	135.2, 134.2, 131.9, 131.5	150.0	41.3	139.4	129.3	128.3	126.2	Ph: 140.8, 128.9(2 C), 127.8(3 C)
(**5c**)	186.2	154.4	135.3, 135.2, 133.4, 132.5	140.3	40.4	138.9	129.2	128.3	126.2	—
(**5d**)	185.5	151.3[b]	134.9, 134.3, 131.8, 131.4	150.0[b]	41.3	139.4	129.2	128.2	126.0	Me: 23.5
(**5e**)	185.5	153.7[b]	134.5, 133.7, 131.8, 131.2	151.7[b]	41.3	139.6	129.2	128.2	126.0	Bu: 36.2, 31.2, 22.7, 13.9
(**5f**)	178.9	148.7	136.2, 130.9, 126.7, 112.0	163.9	41.1	139.6	129.3	128.2	126.1	MeO: 56.1

[a] Recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [b] Chemical shifts are not assigned unequivocally and are interchangeable with each other.

Table 3. Results for the reaction of (**2a–c**), (**3a–c**), and (**4, d**) with TFA

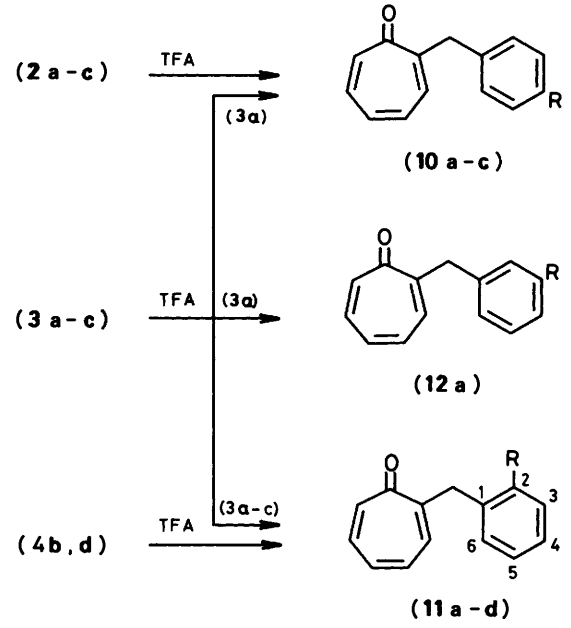
Run	Compound	R	Reaction time (day)	Yield[a] (%) (**10**)	(**11**)	(**12**)	k^b/s^{-1}
1	(**2a**)	4-Bu^t	1	86	0	0	8.6×10^{-4}
2	(**2b**)	4-Ph	1	80	0	0	1.3×10^{-3}
3	(**3a**)	3-Bu^t	1	17	41	14	3.7×10^{-5}
4	(**3b**)	3-Ph	1	0	92	0	4.5×10^{-4}
5	(**2c**) + (**3c**)	3,4-Cl	10	50	23	0	—
6	(**4b**)	2-Ph	2	0	95	0	4.4×10^{-5}
7	(**4d**)	2-OMe	1	0	98	0	$>1.0 \times 10^{-1}$

[a] Reactions were carried out in chloroform in the presence of 3 molar equivalents of TFA at ambient temperature. [b] The rate constants were obtained in carbon tetrachloride at 24 °C in the presence of one molar equivalent of TFA.

derivatives were determined on the basis of ^{13}C NMR (Table 4) and other spectroscopic data, as were compounds (**5d–f**). Satisfactory analytical data were not obtained for the high boiling oils (**10a**), (**11b**), and (**12a**). However, satisfactory high resolution mass spectral data was obtained for them.

Although ^1H NMR spectra of (**3a, b**) supported their formulation as rapidly equilibrating mixtures of CHT and NCD in neutral media,[1] the spectra did not change appreciably in the presence of TFA (1 equiv.), nor did the spectra of (**2a, b**) and (**4b, d**) under identical conditions. Thus, evidence for the existence of the NCD form for (**2a, b**) and (**4b, d**) in acidic media was not obtained. However, the present rearrangements are reasonably explained by the pathways including an NCD intermediate as shown in Scheme 3.

Protonation of (**2a–c**) occurs on the oxygen atom to give (**13a–c**) which may isomerize to the NCD form (**14a–c**). Preferential cleavage of the C(1)–C(2) bond on (**14**) occurred to



Scheme 2.

give (**10a–c**) *via* the stabilized intermediate (**15a–c**), in which the Bu^t, Ph, and Cl groups are located in a conjugated position. The intermediates (**16a–c**), in which the Bu^t, Ph, and Cl groups are in a cross-conjugated position, are less stable compared to (**15a–c**). In the reaction of (**3a–c**), protonation occurs in a similar fashion to give the intermediates (**17a–c**)–(**18a–c**). When R is Ph or Cl,

Table 4. ^{13}C Chemical shifts (ppm) of (**10a–c**), (**11a–d**), and (**12a**)[a]

Compd.	Tropone				Benzyl group							Remaining signals
	C-1	C-2	C-3 to C-6	C-7	CH_2	C-1	C-2	C-3	C-4	C-5	C-6	
(**10a**)	186.5	154.8	135.3, 135.2, 133.5, 132.4	140.5	40.0	135.8	129.0	125.3	149.1	125.3	129.0	Bu^t: 34.4, 31.3(3 C)
(**11a**)	186.6	156.4	135.6, 135.4, 133.4[b], 133.2	139.9	39.2	136.6	148.8	133.3[b]	126.5[b]	126.4[b]	126.0[b]	Bu^t: 35.7, 31.5(3 C)
(**12a**)	186.5	154.9	135.2, 135.2, 133.5, 132.4	140.4	40.6	138.5	126.4[b]	151.3	123.3	128.1	126.6[b]	Bu^t: 34.6, 31.3(3 C)
(**10b**)	186.2	154.2	135.3, 135.2, 133.4, 132.5	140.4	40.2	138.1	129.6	127.0[b]	139.1	127.0[b]	129.6	Ph: 140.6, 128.5(2 C), 126.9, 126.7(2 C)
(**11b**)	186.2	154.7	135.3, 135.0, 133.2, 132.3	139.9	37.7	136.3	142.5	130.4[b]	130.1[b]	127.4	126.7[b]	Ph: 141.2, 127.9(2 C), 128.8(2 C), 126.4[b]
(**10c**)	185.9	153.7	135.3, 135.2, 133.3, 132.7	140.4	40.0	137.4	130.4	128.3	132.0	128.3	130.4	—
(**11c**)	186.2	152.5	135.2, 134.8, 133.3, 132.6	140.1	37.8	136.5	134.5	129.4	127.9	126.7	131.6	—
(**10d**)	186.6	154.2	135.0, 134.5, 133.5, 132.1	140.4	34.6	127.1	157.5	110.4	127.8	120.5	131.2	MeO: 55.2

[a] Recorded in $CDCl_3$ using $SiMe_4$ as internal standard. [b] Interchangeable with each other.

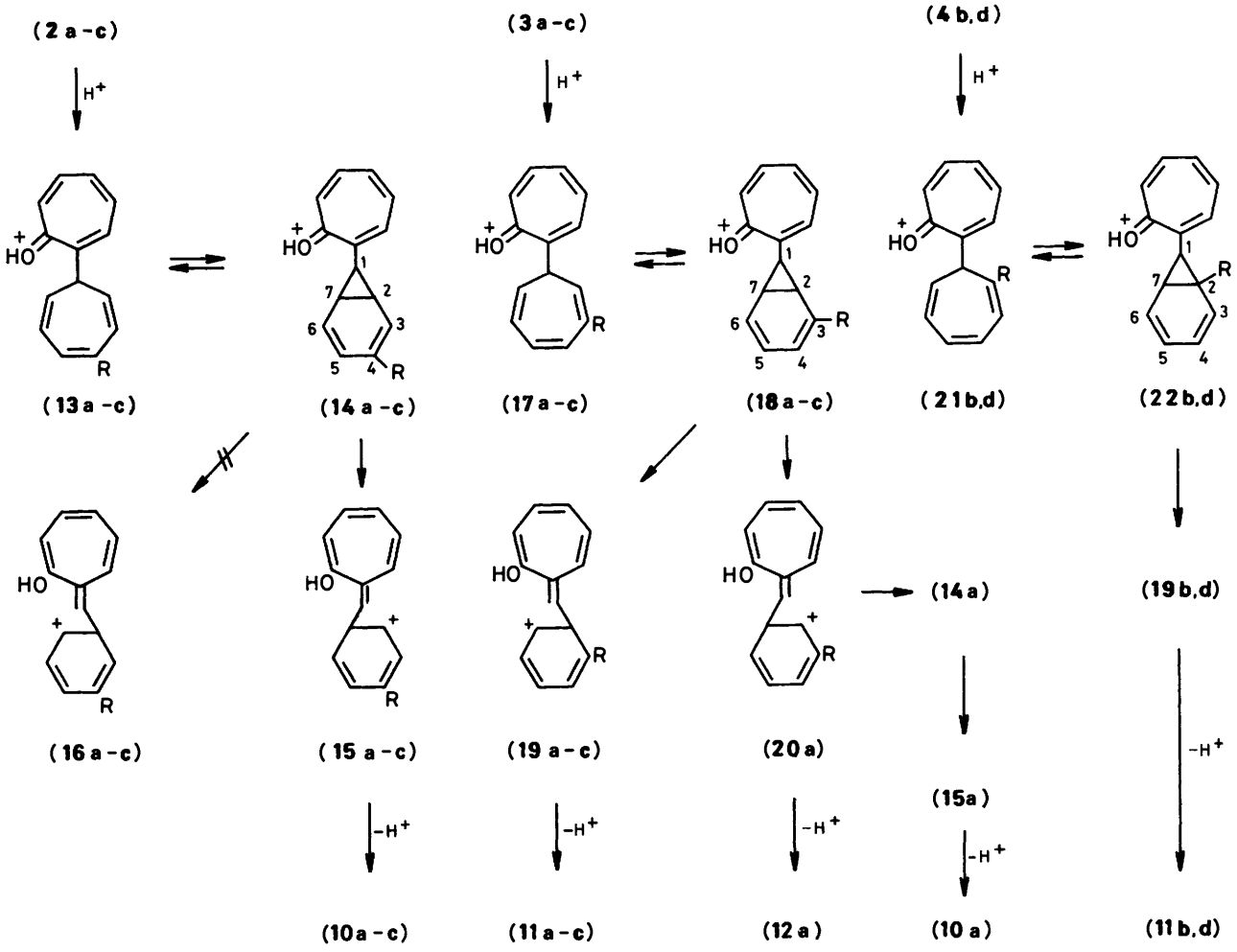
the cleavage of the C(1)–C(7) bond in (**18b, c**) occurs to give (**11b, c**) *via* the intermediates (**19b, c**), in which R is fully conjugated with the cationic centre. In the reaction of (**3a**) (R = Bu^t), cleavage of both the C(1)–C(7) and C(1)–C(2) bond occurs to give (**19a**) and (**20a**). The intermediates (**19a**) and (**20a**) collapse to give (**11a**) and (**12a**), respectively. In addition, intermediate (**20a**) (R = Bu^t) rearranges by a different pathway to give NCD (**14a**), which then easily gives (**10a**) *via* (**15a**). In the reaction of (**4b, d**), C(1)–C(2) bond cleavage occurs exclusively to give (**11b, d**) *via* the more stabilized cation (**19b, d**), the cationic centre of which is stabilized directly by the substituent R (R = Ph and OMe).

As for compounds (**1a–f**), the reaction of (**2a, b**), (**3a, b**), and (**4b, d**) with TFA in carbon tetrachloride at 24 °C also followed first-order kinetics [the observed rate constants (k) are summarized in Table 3]. The rate of reaction of (**4d**) was such that the rate constant could not be determined exactly at this temperature, an estimated value is listed in Table 3. The observed reaction rate of the isomerization for each pair of (**2a, b**), (**3a, b**), and (**4b, d**) is in the order of (**2a**) < (**2b**), (**3a**) < (**3b**), and (**4b**) < (**4d**). Rate constants for these compounds are larger than those of (**1c**), which has no substituent on the cycloheptatriene ring. Regarding the equilibrium between CHT–NCD, compounds (**3a**) and (**3b**) exist as equilibrating mixtures of CHT and NCD even at room temperature. According to their ^1H NMR spectra, the content of the NCD form was estimated to be larger in (**3a**) than in (**3b**).[1] However, the rate constant for (**3a**) is much smaller than that of (**3b**). The reaction rate of the present isomerization may depend on the stability of the carbocation intermediate. A phenyl substituent would stabilize the cationic intermediates (**15**) and (**19**) as compared to a Bu^t group, and the MeO group seems to stabilize the intermediate (**19**) as compared to a Ph group. Thus, the reaction rate of isomerization is dependent on the facility of cleavage of the C–C bond of the NCD form to give carbocation intermediates.

In conclusion, 2-cyclohepta-2,4,6-trienyltropone derivatives were isomerized easily to 2-benzyltropones in acidic media plausibly *via* their norcaradiene intermediates. The selectivity of C–C bond cleavage of the norcaradiene intermediate is much affected by the stabilizing effect of the substituent on the cycloheptatriene ring. The first-order rate of rearrangement was shown to depend on the nature of the substituents both on C-7 of the tropone nucleus and on the cycloheptatriene ring.

Experimental

General Procedure for the Reaction of (**1a–f**) *with Trifluoroacetic Acid (TFA).*—A solution of (**1a–f**) (0.5 mmol) and TFA (570 mg, 5 mmol) in dry chloroform (1 ml) was stirred for 0.5–20 days at ambient temperature. After the solution was diluted with benzene (5 ml), it was neutralized with aqueous $NaHCO_3$. The solution was extracted with benzene, and the extract was dried (Na_2SO_4) and the solvent evaporated. The residue was purified by TLC on silica gel using hexane–ethyl acetate (1 : 1 ⟶ 10 : 1) as developer to give the 2-benzyltropone



Scheme 3.

derivatives. The yields of the products are summarized in Table 1.

(**5a**), pale yellow crystals, m.p. 77–78 °C (from benzene–hexane, 1:5); $\delta_H(CDCl_3)$ 4.02 (2 H, s), 6.71 (1 H, br t, *J* 9.5 Hz), 6.85–7.33 (7 H, m), and 8.09 (1 H, d, *J* 9.2 Hz); $\nu_{max}(CHCl_3)$ 1 620 and 1 593 cm^{-1}; *m/z* 276 (M^+, 65%), 274 (M^+, 66), and 165 (100) (Found: C, 61.1; H, 4.0. $C_{14}H_{11}BrO$ requires C, 61.11; H, 4.03%) [(HRMS) M^+, 274.0024. $C_{14}H_{11}BrO$ requires *M*, 273.9993].

(**5b**), yellow crystals, m.p. 61–62 °C (from benzene–hexane, 1:1); $\delta_H(CDCl_3)$ 4.03 (2 H, s), 6.73–6.91 (2 H, m), 6.91–7.20 (2 H, m), 7.25 (5 H, s), and 7.33 (5 H, s); $\nu_{max}(CHCl_3)$ 1 622 and 1 583 cm^{-1}; *m/z* 272 (M^+, 87%) and 271 (100) (Found: C, 88.1; H, 6.0. $C_{20}H_{16}O$ requires C, 88.20; H, 5.92%) [(HRMS) M^+, 272.1183. $C_{20}H_{16}O$ requires *M*, 272.1201].

(**5c**),[17] pale yellow oil; $\delta_H(CDCl_3)$ 3.94 (2 H, s), 6.74–6.91 (2 H, m), 6.91–7.15 (3 H, m), and 7.23 (5 H, s); $\nu_{max}(CHCl_3)$ 1 630 and 1 583 cm^{-1}.

(**5d**), yellow oil; $\delta_H(CDCl_3)$ 2.29 (3 H, s), 4.00 (2 H, s), 6.59–6.92 (2 H, m), 7.00–7.35 (2 H, m), and 7.23 (5 H, s); $\nu_{max}(CHCl_3)$ 1 624 and 1 565 cm^{-1}; *m/z* 210 (M^+, 100%) [(HRMS) M^+ 210.1059. $C_{15}H_{14}O$ requires *M*, 210.1045].

(**5e**), pale yellow oil; $\delta_H(CDCl_3)$ 0.90 (3 H, br t, *J* 6.4 Hz), 1.08–1.70 (4 H, m), 2.68 (2 H, br t, *J* 7.3 Hz), 4.00 (2 H, s), 6.71–6.88 (2 H, m), 6.90–7.30 (2 H, m), and 7.23 (5 H, s); $\nu_{max}(CHCl_3)$ 1 620 and 1 574 cm^{-1}; *m/z* 252 (M^+, 100%) [(HRMS) M^+, 252.1503. $C_{18}H_{20}O$ requires *M*, 252.1515].

(**5f**), pale yellow oil; $\delta_H(CDCl_3)$ 3.88 (3 H, s), 4.07 (2 H, s), 6.50–7.32 (4 H, m), and 7.24 (5 H, s); $\nu_{max}(CHCl_3)$ 1 596 and 1 563 cm^{-1}; *m/z* 226 (M^+, 100%) [(HRMS) M^+, 226.0983. $C_{15}H_{14}O_2$ requires *M*, 226.0994].

General Procedure for the Reaction of (**2a, b**), (**3a, b**), *and* (**4b, d**) *with TFA.*—A solution of (**2a, b**), (**3a, b**), and (**4b, d**) (0.3 mmol) and TFA (103 mg, 0.9 mmol) in dry chloroform (0.6 ml) was stirred for 1–2 days at ambient temperature. After the usual work-up described above, the product was purified by TLC on silica gel using hexane–ethyl acetate (3:1 ⟶ 7:1) as a developer to give the corresponding 2-benzyltropone derivatives. The yields of the products are summarized in Table 3.

(**10a**), pale yellow oil; $\delta_H(CDCl_3)$ 1.31 (9 H, s), 3.94 (2 H, s), 6.63–7.35 (5 H, m), 7.17 (2 H, d, *J* 8.2 Hz), and 7.32 (2 H, d, *J* 8.2 Hz); $\nu_{max}(CHCl_3)$ 1 630 and 1 575 cm^{-1}; *m/z* 252 (M^+, 100%) and 237 (100) [(HRMS) M^+, 252.1525. $C_{18}H_{20}O$ requires 252.1514].

(**10b**), pale yellow crystals, m.p. 88–90 °C (from ethanol); $\delta_H(CDCl_3)$ 3.97 (2 H, s) and 6.70–7.65 (14 H, m); $\nu_{max}(CHCl_3)$ 1 634 and 1 574 cm^{-1}; *m/z* 272 (M^+, 100%) (Found: C, 88.0; H, 6.05. $C_{20}H_{16}O$ requires C, 88.20; H, 5.92%) [(HRMS) M^+, 272.1193. $C_{20}H_{16}O$ requires *M*, 272.1201].

(**11a**), pale yellow crystals, m.p. 86–89 °C (from benzene–hexane, 1:10); $\delta_H(CDCl_3)$ 1.27 (9 H, s), 4.17 (2 H, s), 6.56–7.25 (8 H, m), and 7.25–7.46 (1 H, m); $\nu_{max}(CHCl_3)$ 1 632 and 1 569 cm^{-1}; *m/z* 252 (M^+, 10%) and 143 (100) (Found: C, 85.65; H, 8.0. $C_{18}H_{20}O$ requires C, 85.67; H, 7.99%) [(HRMS) M^+, 252.1553. $C_{18}H_{20}O$ requires *M*, 252.1514].

(**11b**), pale yellow oil; $\delta_H(CDCl_3)$ 3.95 (2 H, s), 6.65–7.15 (4 H, m), and 7.26 (10 H, s); $\nu_{max}(CHCl_3)$ 1 631 and 1 571 cm^{-1}; *m/z*

272 (M^+, 100%) [(HRMS) M^+, 272.1223. $C_{20}H_{16}O$ requires 272.1201].

(**11d**), pale yellow crystals, m.p. 73–74 °C (from hexane); $\delta_H(CDCl_3)$ 3.75 (3 H, s), 3.96 (2 H, s), and 6.72–7.32 (9 H, m); $\nu_{max}(CHCl_3)$ 1 630 and 1 567 cm^{-1}; *m/z* 226 (M^+, 74%) and 120 (100) (Found: C, 79.6; H, 6.4. $C_{15}H_{14}O_2$ requires C, 79.62; H, 6.24%) [(HRMS) M^+, 226.0986. $C_{15}H_{14}O_2$ requires *M*, 226.0994].

(**12a**), pale yellow oil; $\delta_H(CDCl_3)$ 1.31 (9 H, s), 3.97 (2 H, s), and 6.64–7.33 (9 H, m); $\nu_{max}(CHCl_3)$ 1 631 and 1 573 cm^{-1}; *m/z* 252 (M^+, 100%) [(HRMS) M^+, 252.1525. $C_{18}H_{20}O$ requires *M*, 252.1514].

The Reaction of a Mixture of (**2c**) *and* (**3c**) *with TFA.*—A solution of a mixture of (**2c**) and (**3c**) in a ratio of 65:35 (161 mg, 0.7 mmol) and TFA (798 mg, 7 mmol) in dry chloroform (1.4 ml) was stirred for 10 days at ambient temperature. After the work-up described above, the product was purified by TLC on silica gel using hexane–ethyl acetate (5:1) as a developer to give (**10c**) (81 mg, 50%) and (**11c**) (38 mg, 23%).

(**10c**), colourless crystals; m.p. 74–75 °C (from benzene–hexane, 1:10); $\delta_H(CDCl_3)$ 3.89 (2 H, s), 6.75–7.30 (5 H, m), and 7.19 (4 H, s); $\nu_{max}(CHCl_3)$ 1 633 and 1 574 cm^{-1}; *m/z* 232 (M^+, 33%) and 230 (M^+, 100) (Found: C, 72.25; H, 4.8. $C_{14}H_{11}ClO$ requires C, 72.89; H, 4.81%) [(HRMS) M^+, 230.0506. $C_{14}H_{11}ClO$ requires *M*, 230.0498].

(**11c**), colourless crystals, m.p. 68–69 °C (from benzene–hexane 1:10); $\delta_H(CDCl_3)$ 4.08 (2 H, s) and 6.68–7.50 (9 H, m); $\nu_{max}(CHCl_3)$ 1 632 and 1 573 cm^{-1}; *m/z* 232 (M^+, 1%), 230 (M^+, 3) and 195 (100) (Found: C, 72.8; H, 4.8. $C_{14}H_{11}ClO$ requires C, 72.89; H, 4.81%) [(HRMS) M^+, 230.0500. $C_{14}H_{11}ClO$ requires *M*, 230.0498].

Reaction Rate of 2-Cyclohepta-2,4,6-trienyltropone Derivatives (**1a–f**), (**2a**, **b**), (**3a**, **b**), *and* (**4b**, **d**).—2-Cyclohepta-2,4,6-trienyltropone derivatives (0.15 mmol) were placed in a ^1H NMR tube and carbon tetrachloride was added until the volume of the solution reached 0.138 cm^3. At 24 °C, TFA (11.6 μl, 0.15 mmol) was added and the mixture was shaken vigorously. The ^1H NMR spectrum of the solution was recorded on a Hitachi R-24 spectrometer. The concentration ratio of the starting material and isomerized products were calculated from the signals ascribed to the 7-H in cycloheptatriene ring and the benzylic protons of the product. The results thus obtained are summarized in Tables 1 and 3.

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