Tetrahedron. Vol. 27, pp. 4013 to 4020. Pergamon Press 1971. Printed in Great Britain

REACTIONS OF DEHYDROBENZENE—III

THE REACTIONS WITH SUBSTITUTED TROPONES AND N-TRICHLOROACETYLTROPONIMINE

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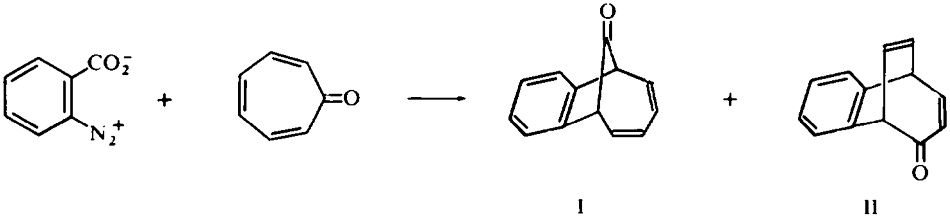
(*Received in Japan* 15 *February* 1971; *Received in the UK for publication* 3 *May* 1971)

Abstract—The reactions of α-chloro-, α-bromo-, α-methoxy-, and α-hydroxy-tropones and N-trichloroacetyltroponimine with dehydrobenzene are described.

IN A previous communication of this series, we described the reaction of dehydrobenzene with tropone to give a 1,6-cycloaddition product[1] besides a 1,4-cycloaddition product, which had been reported initially by Ciabattoni and Kende.[2]



SCHEME 1

Recent interests on the photochemical reactions of the above products [3–6] prompt us to report the results of the reactions of dehydrobenzene with substituted tropones and N-trichloroacetyltroponimine.

It is well known that tropones react with ordinary dienophiles to give Diels–Alder type addition products,[7–10] but with activated olefins such as ketene to give 1,3-dipolar adducts.[11]

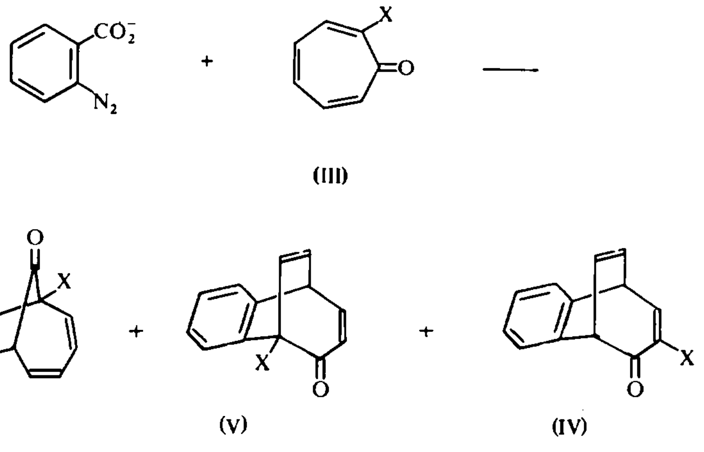
On the other hand, Jones and Levin proved that (2 + 2)π cycloadditions of dehydrobenzene with olefins are non-stereospecific, while (2 + 4)π cycloadditions with relatively reactive dienes are completely stereospecific, hence orbital symmetry considerations predict that the structure of *o*-benzyne is symmetric singlet in its ground state.[12]

As mentioned above, we found that tropone undergoes with dehydrobenzene not only 2 + 4 cycloaddition but also a 2 + 6 reaction. Although yields varied by alteration of solvents, the ratios of the two products remained unchanged, accordingly both products were formed in a non-ionic process.[13]

Thus, it was interesting for us to investigate the effect of substituents in the tropone ring upon reaction courses and the relative reactivities of tropones with dehydrobenzene. Among the tropones, α-chloro-, α-bromo-, α-methoxy-, and α-hydrooxytropones were used and allowed to react independently with benzenediazonium *o*-carboxylate (prepared from 1·05 molar equivalent of anthranilic acid[14]) by heating in dioxane.

The reaction of α-chlorotropone with dehydrobenzene gave three crystalline products, A, B and C, which were separated by column chromatography. The structure (VIa) of compound A, mp. 111–113°, was deduced from spectra, λ_{max}^{EtOH} nm. (log. ε) 265^{sh} (3·43), 273 (3·53), 279 (3·52); $\nu^{liq. film}$ 1770 cm^{-1}; δ ppm. 3·97 (1H, d. J = 7 Hz.), 5·5–6 (4H, m); these spectra are comparable with those of 7,8-benzobicyclo[4.2.1]-nona-2,4,7-trien-9-one (I), λ_{max}^{EtOH} $262^{infl.}$, 270, 277 nm.; $\nu_{max}^{CCl_4}$ 1766 cm^{-1}; δ ppm. 3·85 (2H, d. J = 8 Hz.), 5.6–6.1 (4H, m).

Products B and C have α,β-unsaturated carbonyl grouping ($\nu_{C=O}$ 1678 and 1686 cm^{-1} respectively) and their NMR spectra are quite similar to that of 6,7-benzobicyclo[3.2.2]nona-3,6,8-trien-2-one (II) except lack of the peaks due to 3-H and 1-H respectively, hence they should carry chlorine atoms at these positions (IVa and Va). The UV spectra also support these structures[15]; that is, compound B showed the UV maximum at 244 nm. (log ε 3·79), just as the calculated value (241 nm.) for α-chloro-α,β-unsaturated ketone, but compound C had no absorption maximum above 220 nm.



Scheme 2

Likewise, structures of compounds IVb–c, Vb–d, and VIb–c were determined; their physical constants are listed in Table I and II.

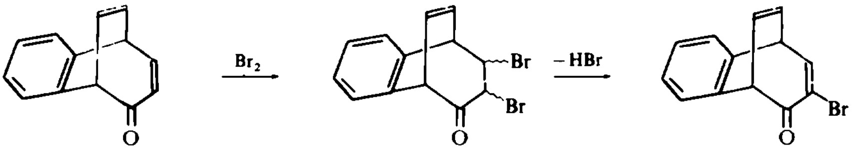
Furthermore, IVb was identified with a product derived from the ketone (II) by two steps, bromination followed by dehydrobromination.

Table I shows that the substituents have a considerable influence upon the yields of 1,4-cycloaddition products, while not upon those of 1,6-cycloaddition products.

It should be mentioned here that tropolone reacts with benzenediazonium *o*-carboxylate in dioxane to give, besides the 1,4-addition product (Vd), a considerable

TABLE I. THE PRODUCTS AND THEIR YIELDS OBTAINED BY THE REACTION OF α-SUBSTITUTED TROPONES AND DEHYDROBENZENE

Starting tropones	Cycloaddition products					
(III)	(V)	%	(IV)	%	(VI)	%
a, X = Cl	mp. 84·5–85°	34·5	mp. 111·5–112°	24	mp. 111–113°	2
b, X = Br	mp. 119·5–120·5°	44	mp. 116–117°	29		trace
c, X = OCH_3	mp. 128·5–129·5°	68	mp. 114–115°	7		trace
d, X = OH	mp. 108·5–109·5°	24	—	—		—



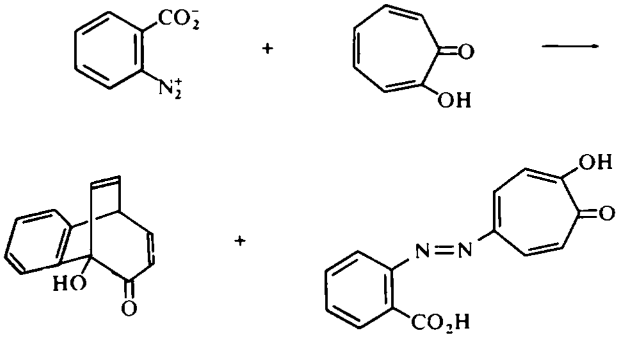
(II) (IVb)

SCHEME 3

TABLE II. THE IR AND NMR SPECTRA OF THE 1,4-CYCLOADDITION PRODUCTS OF DEHYDROBENZENE TO α-SUBSTITUTED TROPONES

Compounds	IR spectra $\nu_{max}^{nujol\,mull}$ cm^{-1}		NMR spectra δ ppm. ($CDCl_3$)			
			5-H	1-H	3-H	OCH_3
(IVa)	1678(s) 1621(m) 1590(w)	1318(m)	4·33	4·86	—	
(Va)	1687(s) 1625(w)	1370(m) 1230(m)	4·33	—	5·42	
(IVb)	1672(s) 1625(m) 1582(m)	1308(m)	4·28	4·84	—	
(Vb)	1674(s) 1625(w)	1367(m) 1230(m)	4.28	—	5·38	
(IVc)	1675(s) 1627(m) 1606(2)	1213(s) 1148(s) 1120(s)	4·30	4·70	—	3·39
(Vc)	1678(s) 1630(m)	1342(m) 1215(m) 1112(s)	4.30	—	5·22	3.53
(Vd)	3460(s) 1662(s) 1625(m)	1295(mb) 1212(s) 1105(s)	4.36	—	5.46	

amount of dichloromethane-insoluble, reddish brown crystals, $C_{14}H_{10}O_4N_2$, m.p. 210–210·5° (dec.). The same substance was obtained in good yield by the reaction in a phosphate buffer of pH 6·9 at a low temperature.[16] Since the visible regions of the electronic spectra of the substance in alkaline and acidic media ($\lambda_{max}^{EtOH(NaOH)}$ 402, 450 nm., $\lambda_{max}^{EtOH(HCl)}$ 382, 480$^{infl.}$ nm.) were similar to those of 5-phenylazotropolone ($\lambda_{max}^{EtOH(NaOH)}$ 4·5, 462 nm., $\lambda_{max}^{EtO(HCl)}$ 385 nm.), this compound must be 5-(*o*-carboxyphenylazo)tropolone (VII); this was confirmed by its hydrogenolysis to 5-aminotropolone[17] and anthranilic acid.



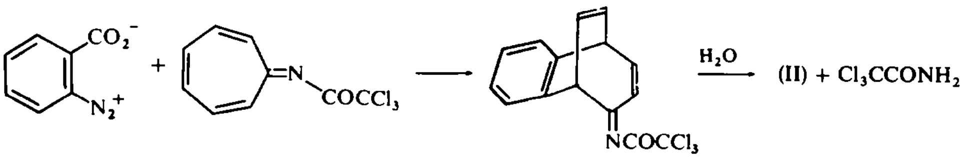
(Vd) (VII)

Scheme 4

We could not detect any compound produced by the attack of dehydrobenzene at oxygen of tropolone, usually observed by the reaction of dehydrobenzene with an alcohol or a phenol,[18] or at 5-position, as was seen in the case of the reaction of diethyl azodicarboxylate with tropolone.[19]

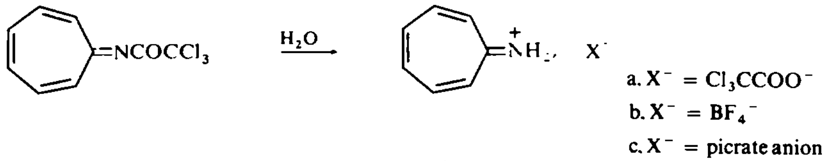
In order to obtain further information on the reactivity of dehydrobenzene towards troponoids, the reaction of a reactive troponimine, N-trichloroacetyltroponimine[20] with benzenediazonium *o*-carboxylate in dry CH_2Cl_2 was carried out. From aq. $NaHCO_3$ extract of the reaction, we isolated a small amount of trichloroacetic acid and *o*-chlorobenzoic acid. The neutral fraction of the products was chromatographed on Florisil giving trichloroacetamide and a mixture of two components from which the ketone (II) was isolated. The NMR of the mixture inferred that the other component might be 2-(N-trichloroacetylimino)-6,7-benzobicyclo[3.2.2]nona-3,6,8-triene (IX) having the same structural framework as II. Although the isolation of IX has not been achieved because of its ready hydrolysis under chromatographic conditions, the presence was confirmed by hydrolysis of the mixture separated from trichloroactamide to give the ketone II and the amide, both in good yields.

It is worth noting here that the troponimine(VIII) is sensitive to H_2O. When it was stirred in wet ether, a large quantity of pale gray crystals gradually precipitated. Recrystallization gave a pure sample, $C_9H_8NO_2Cl_3$, m.p. > 360°. Its UV and NMR spectra resemble closely those of tropylideneimmonium fluoroborate (Xb), prepared by the method of Dauben,[21] and the picrates derived from both salts were identical in every respect.



(VIII) (IX)

SCHEME 5



(X)

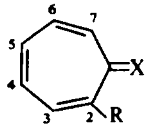
SCHEME 6

These observations indicate that these precipitates must be tropylideneimmonium trichloroacetate (Xa), and the above method has synthetic utility for the salt.

From the above experiments, it is clear that dehydrobenzene reacts with the troponimine almost solely in 1,4-cycloaddition manner (*ca.* 40%) and the adduct was then partially hydrolyzed during isolation steps.

Next, in order to study the relative reactivities of the troponoids in the above 1.4-cycloaddition reaction with dehydrobenzene, each one molar equivalent of tropone, any one of the troponoids above mentioned and benzenediazonium *o*-carboxylate were allowed to react by heating in dioxane at 50°, and the neutral fraction from the reaction examined carefully by NMR spectroscopy to estimate the compositions of the Diels–Alder type products.

TABLE III. THE RELATIVE REACTIVITIES OF THE DIENE FUNCTION IN α-SUBSTITUTED TROPONES TOWARDS DEHYDROBENZENE



Troponoids	Cycloaddition to	
	2.5-positions	4.7-positions
X = O, R = H	1·0	1·0
X = O, R = Cl	1·5	1·0
X = O, R = OCH_3	3·0	0·4
X = O, R = OH	6·0	—
X = $NCOCCl_3$, R = H	1·1	1·1

The product ratios thus obtained are expressed as relative reactivities, which are respectively the yields of addition products at one of the 2,5- and 4,7-positions of the substituted tropones relative to the yield of product at one of the two equivalent 2,5-positions in tropone. In the case of the troponimine, the competition reaction against α-chlorotropone, in place of tropone, was carried out and the product ratio obtained after hydrolysis of the neutral fraction. The data obtained are in Table III.

It is interesting to note that the relative reactivities of the diene functions are roughly proportional to the yields of the products obtained by the reaction where one of the tropones was treated with benzenediazonium *o*-carboxylate in an equivalent ratio. In the case of tropolone, the parallelism is not seen. This might be caused by the following reasons; (a) there exists another much faster ionic reaction pathway leading to (VII) and (b) the reaction mechanism could be different, as observed by Ito *et al.*[8], from those of concerted 2 + 4 cycloaddition reaction.

From this table, it is obvious that the substituents enhance the reactivity of the diene towards the Diels–Alder reaction where they are directly attached, but the alteration of the oxygen of tropone to a trichloroacetylimino function does not affect the reactivity.[22]

Acknowledgement—The authors are grateful to Mr. J. Goda for the analytical data, and to Messrs. T. Matsukura and T. Sawa for their skillful technical assistance. The authors wish to thank Dr. G. Sunagawa, the Director of the Sankyo Central Laboratory, for a generous supply of tropone, and Dr. Y. Hirose of the

EXPERIMENTAL

All m.ps are uncorrected. IR spectra were measured on a Hitachi IR-E spectrophotometer. UV spectra were measured on a Hitachi EPS-2 spectrophotometer. NMR spectra were measured on a JEOL C-60 spectrometer with TMS as an internal standard. Chemical shifts are expressed in ppm from TMS.

Benzenediazonium o-carboxylate. To an ice cooled, stirred solution of anthranilic acid (2·0 g., 14·6 mM.) in 20 ml. of dry THF containing *ca.* 40 mg. of trichloroacetic acid, n-butyl nitrite (2·9 g., 28 mM.) was added dropwise over 15 min. The cooling and stirring were continued for one hr. The resulting solution being kept overnight in a refrigerator, pale brown precipitates of the salt were formed and filtered. After washing with cold CH_2Cl_2 and cold Et_2O, the salt was used immediately without thorough drying.

Reactions of benzenediazonium o-carboxylate with troponoids: (a) *with α-chlorotropone.* Benzenediazonium *o*-carboxylate prepared as above was decomposed in 40 ml. of dry dioxane containing 2·1 g. (14·9 mM.) of α-chlorotropone by warming at 50° for 3 hr.; 520 ml. (72% of the theoretical) of gas was evolved and collected. The red solution was concentrated to dryness, dissolved in CH_2Cl_2, washed successively with 5% aq. Na_2CO_3, H_2O saturated NaCl aq. and dried with anhyd Na_2SO_4. The residue (3·3 g.) was chromatographed. (C_6H_6) on silica (80 g.); 80-ml. fractions collected. Fraction 3 contained 0·66 g. solid, rechromatographed with n-hexane-ether (5:1 v/v), on 33 g. of silica; (33-ml. fractions). Fractions 5 and 6 contained 0·48 g of solid recrystallized from n-hexane; colorless crystals (IVa): m.p. 111·5–112·5. (Calc. for $C_{13}H_9OCl$: C, 72·05; H, 4·19. Found: C, 72·25; H, 4·20%). Fraction 4 of the second chromatography was further separated, hexane-ether (5:1 v/v), on 4 g. of silica (4 ml. fractions). Repeated chromatography on silica of the 4th fraction gave 20 mg. solid. Sublimation and recrystallization from MeOH gave colorless needles (VIa), m.p. 111–113°. Mass spectrum, *m/e*; 218(3·00), 216(9·42), 190(5·1), 188(14·7), 181 (38·5), 153(100), 152(55·9).

Fractions 4–7 of the initial chromatography contained 1·20 g. of solid rechromatographed on silica (60 g.) hexane-ether (5:1); (60-ml. fractions). Besides 0·20 g. of IVa from Fr. 4 and 5, 0·81 g. of colorless crystals obtained from fractions 6–9 recrystallized twice from n-hexane; colorless crystals (Va), m.p. 84·5–85°. (Calc. for $C_{13}H_9OCl$: C, 72·05; H, 4·19. Found: C, 72·23; H, 4·24%).

(b) *with α-bromotropone.* The same reaction conditions described for α-chlorotropone used with 2·80 g. (15 mM.) of α-bromotropone instead of α-chlorotropone. Usual work-up gave, besides (VIb) as an orange oil (26 mg.), two crystalline products; pale yellow leaflets (Vb), 1·55 g, m.p. 119·5–120·5° (n-hexane), and pale yellow crystals (IVb), m.p. 116–117° (n-hexane). (Calc. for $C_{13}H_9OBr$: C, 59·80; H, 3·47. Found: (Vb); C, 60·03; H, 3·60: (IVb); C, 59·98; H, 3·59%).

(c) *with tropolone methyl ether.* A mixture of benzenediazonium *o*-carboxylate, prepared from 4·1 g. (30 mM.) of anthranilic acid, and tropolone methyl ether (4·1 g., 30 mM.) in 80 ml. of dioxane was allowed to react as above. The solid neutral fraction (6·44 g.) from the mixture was chromatographed, C_6H_6-Et_2O (9:1 v/v), on 120 g. silica. The first 240 ml. of effluent was concentrated and the crystalline residue washed with Et_2O; yellow crystals, 2·4 g. (Vc). The residue from the ethereal solution (0·31 g.) was rechromatographed on 15 g. of Florisil. Elution with CH_2Cl_2, (15-ml fractions). Fraction 3 contained 137 mg. pale yellow crystals. Recrystallization from n-hexane gave colorless crystals (IVc). m.p. 114–115°. (Calc. for $C_{14}H_{12}O_2$: C, 79·22; H, 5·70. Found: C, 79·23; H, 5·78%).

The second 240 ml. effluent of the initial chromatography contained 2·1 g. yellow solid, which was mixed with the crystals from the first 240-ml. fraction and recrystallized from C_6H_6 and gave pale yellow crystals (Vc), m.p. 128·5–129·5°. (Calc. for $C_{14}H_{12}O_2$: C, 79·22; H, 5·70. Found: C, 79·36; H, 5·83%).

(d) *with tropolone.* Benzenediazonium *o*-carboxylate, prepared from 5·63 g. (41 mM.) of anthranilic acid. was decomposed in 100 ml. of dry dioxane contained 5·0 g. (41 mM.) of tropolone. The red residue from the mixture was digested with CH_2Cl_2 (50 ml.) and the insoluble materials (1·1 g.) filtered and recrystallized from MeOH; reddish brown crystals (VII). m.p. 210–210·5° (dec.). (Calc. for $C_{14}H_{10}O_4N_2$: C, 62·22; H, 3·73; N, 10·37. Found: C, 61·97; H, 3·98; N, 10·04%). λ_{max}^{EtOH} (log ε) 225(4·45), 384(4·28), 524(3·91) nm.; $\nu_{max}^{Nujol\ mull}$ cm^{-1} 3180^b, 1710, 1620, 1592^m, 1570^m; δ ppm. (CF_3COOH) 7·75–9·00 (complex multiplets).

The filtrate was washed with 5% $NaHCO_3$ aq., H_2O and dried with anhyd. Na_2SO_4. The residue (4·71 g.), showed only strong peaks due to (Vd) (NMR spectrum), was chromatographed on 93 g. silica, with $CHCl_3$ (93-ml. fractions). Fractions 2–4 gave 1·94 g. of yellow solid, rechromatographed on silica (40 g.), with $CHCl_3$; (40-ml. fractions), fractions 3–5 contained 1·5 g. of pale yellow solid. Recrystallization from EtOH gave 0·91 g. of colorless crystals (Vd), m.p. 108–109·5°. (Calc. for $C_{13}H_{10}O_2$: C, 78·77; H. 5·09. Found: C, 78·93; H, 5·11%).

(e) *with* N-*trichloroacetyltroponimine.* Benzenediazonium *o*-carboxylate, prepared from 2·7 g. (20 mM.) anthranilic acid, was decomposed in anhyd. CH_2Cl_2 containing 5·0 g. (20 mM.) of N-trichloroacetyltroponimine.[20] After stirring and warming at 30–35 for 2·5 hr (1·0 l. of gas evolved). the mixture was successively washed with H_2O, 5% $NaHCO_3$ aq., H_2O and sat. NaCl aq. After drying, the solution was concentrated to dryness. NMR of the residue (4·9 g.) revealed it contained (IX) and (II) in a ratio of 2·5:1. The residue was chromatographed. ($CHCl_3$). on 100 g. of Florisil; (25-ml. fractions). Fractions 5. 6–7. and 8–11 contained 0·38 g. ((IX):(II) = 3:1), 3·1 g. ((IX):(II) = 1:1) and 0·29 g. (II) of the products respectively. Further chromatographic separation of the fraction 5 did not improve separation. Fractions 12–23 gave 0·54 g. of trichloroacetamide.

Hydrolysis of the mixture (II) *and* (IX). A mixture of compounds (II) and (IX) from fractions 6–11 of the above chromatography, was stirred in 50 ml. Et_2O containing 1 ml. 1N HCl for 5 hr at room temp. and the ethereal solution washed with H_2O, sat. NaCl aq. and dried with anhyd. Na_2SO_4. After evaporation of Et_2O, the residue, taken up in 5-ml. $CHCl_3$ was filtered from insoluble colorless leaflets, 0·29 g., m.p. 138–139·5°, identified with authentic sample of trichloroacetamide. The $CHCl_3$ solution was concentrated to dryness giving 2·37 g. (65%) of colorless semisolid. Recrystallization from n-hexane gave the ketone (II), colorless crystals; m.p. 79·5–81°.

Hydrolysis of N-*trichloroacetyltroponimine*; *tropylideneimmonium trichloroacetate* (Xa). A mixture of N-trichloroacetyltroponimine (1·0 g., 4 mM.), 0·15 ml. of H_2O and a few crystals of trichloroacetic acid in 20 ml. of Et_2O was stirred for 32 hr at room temperature. A pale gray precipitate (730 mg. 68%) was obtained m.p. > 360°. Recrystallization from CH_2Cl_2 gave pale gray powder-like crystals (Xa). (Calc. for $C_9H_8NO_2Cl_3$: C, 40·25; H, 3·00; N, 5·22. Found: C, 40·55; H, 3·09; N, 5·73%). $\nu_{max}^{nujol\ mull}$ cm^{-1}, 3160^{sh}, 2700^{sh}, 1675, 1650^{sh}, 1525. 1460, 1380, 1320. λ_{max}^{EtOH} (log. ε) 233(4·37), 237·5 (4·38), 240·5(4·37), 248·5$^{infl.}$ (4·13), 328(4·20) nm. δ ppm. (D_2O) 7·45–8·25 (complex multiplets). When aq. solution of picric acid was added to the crude precipitates dissolved in H_2O. a picrate precipitated as golden yellow crystals, recrystallized from MeOH; bright orange needles (Xc), m.p. 192–193°. identified with the sample of tropylideneimmonium picrate (*loc. cit.*) m.ps and IR. (Calc. for $C_{13}H_{10}N_4O_7$: C, 46·71; H, 3·02; N, 16·76. Found: C, 46·90; H, 3·14; N, 16·65%). $\nu_{max}^{Nujol\ mull}$ cm^{-1} 3360^s, 1670^m, 1640^{sh}, 1630^{vs}, 1610^{sh}.

Authentic tropylideneimmonium picrate (Xc). To tropylideneimmonium fluoroborate, prepared by the method of Dauben,[21] dissolved in H_2O, excess of aq. picric acid was added. The golden yellow picrate was recrystallized from MeOH bright yellow crystals, m.p. 192–193°.

Competition experiments: Tropone (10 mM.) and a substituted tropone (10 mM.) dissolved in 150 ml. of dioxane were mixed with benzenediazonium *o*-carboxylate prepared from anthranilic acid (10·5 mM.). The mixture was stirred and warmed at 50° for 3 hr. Solvent was evaporated to dryness and the residue taken up in CH_2Cl_2 was washed with 5% $NaHCO_3$ aq. H_2O and then dried with anhyd. Na_2SO_4. The residue was taken up in CCl_4 and evaporated to dryness. The NMR of the residue was taken and the contents of (II). (IV) and (V) were estimated by comparison of the signal areas due to H-1's, H-3's, H-5's protons of the products; (Table III). The ratios were also checked by vpc technique in the cases of chloro- and methoxytropones. but, in either case, no clear-cut resolution between the two products (IV) and (V) was obtained.

5-(o-carboxyphenylazo)-tropolone (VII). Benzenediazonium *o*-carboxylate, prepared from 1·37 g. (10 mM.) of anthranilic acid, dissolved in cold H_2O (50 ml.) was added dropwise to a stirred solution of 1·0 g. of tropolone (8·2 mM.) in 100 ml. of phosphate buffer (pH 6·9) under ice-cooling, and stirring was continued for 2 hr. The red precipitate was filtered and recrystallized from MeOH; reddish brown crystals (840 mg.), m.p. 210–211·5° (dec.), identical with the sample obtained by the above reaction of benzenediazonium *o*-carboxylate with tropolone in dioxane.

Hydrogenolysis of 5-(o-carboxyphenylazo)tropolone (VII). To a solution of 200 mg. of VII dissolved in 5 ml. of 10% NaOH aq. was added portionwise 1·0 g. of sodium hydrosulfite at room temp. and stirred for three hr. The yellow precipitate was dissolved by warming and the resulting yellow solution acidified with conc. HCl and filtered. The filtrate was neutralized with Na_2CO_3 aq. and extracted with C_6H_6, dried with anhyd. Na_2SO_4 and evaporated, to give a yellow solid, the IR spectrum and TLC of which revealed anthranilic acid and 5-aminotropolone; this mixture was sublimed at 100–120°/5 mm Hg. The sublimate (15 mg.) was recrystallized from C_6H_6 to give yellow crystals, m.p. 177–178°, identified by comparison of its m.p., UV and IR spectra (λ_{max}^{EtOH} 234, 361 nm., $\nu_{max}^{nujol\ mull}$ 3340, 3330, 3200 cm^{-1}) with those of 5-aminotropolone, prepared from 5-(p-tolylazo)-tropolone.

3-Bromo-6.7-benzobicyclo [3.2.2]*nona-3.6.8-trien-2-one* (IVb) *from the ketone* (II). To the ketone II (819 mg.; 4·5 mM.) dissolved in CCl_4 (9 ml.) was added a solution of Br_2 (720 mg.; 4·5 mM.) in CCl_4 (14 ml.) at room temp. and the mixture stirred for 5 min. After evaporation of solvent, the residue was recrystallized from C_6H_6; colorless crystals (300 mg.). Repeated recrystallization gave pure dibromide, m.p. 140·5–141·5°. (Calc. for $C_{13}H_{10}OBr_2$: C, 45·67; H, 2·95. Found: C, 45·85; H, 3·00. $\nu_{max}^{Nujol\ mull}$ 1720 cm^{-1}. The crude crystals were boiled in EtOH to give colorless needles (200 mg.). M.p., IR, and NMR spectra were identical with those of the ketone (IVb) obtained from the reaction of α-bromotropone with dehydrobenzene.

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