

2,2,4,4-Tetradeuterioteloidinone.—The procedure described for the preparation of tetradeuteriotropinone was used.

Ethylation of Pseudotropine.—Pseudotropine (1 g.) was dissolved in absolute ethanol (5 cc.). To this solution was added ethyl iodide (1.5 g.). The solution was allowed to stand 24 hours at room temperature. The precipitated crystals were filtered off (1.6 g.), washed with ethanol and dried at 100° (0.1 mm.), dec. p. 321°.

Anal. Calcd. for C₁₀H₂₀O I N (297.19): C, 40.41; H, 6.78; N, 4.71. Found: C, 40.20; H, 6.91; N, 4.49.

Methylation of N-Ethylorpseudotropine.—N-Ethylorpseudotropine (0.5 g.) was treated with methyl iodide (0.7 g.) in ethanol (2.5 cc.). The resulting precipitate was filtered off after 24 hours (0.71 g.) and dried at 100° (0.1 mm.), dec. p. 325–328°.

Anal. Calcd. for C₁₀H₂₀O I N (297.19): C, 40.41; H, 6.78; N, 4.71. Found: C, 40.14; H, 6.71; N, 4.32.

N.m.r. Spectra.—The spectra were measured at room temperature with a Varian V-4300 B spectrometer, equipped with superstabilizer, at 40 Mc. The positions of the bands were measured by the usual sideband technique. As reference toluene served in an external annulus. The spectra were measured in 20–25% (w./v.) solutions and the chemical shifts reported are not corrected to zero concentration. Values for the equilibrium constants were obtained by recording the spectra with a Varian G 10 recorder. The peak areas were cut out and measured by weighing. The values reported are the average of ten determinations for each compound.

CHICAGO 37, ILL.

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Electrophilic Fragmentation in the Tropilidene Series

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This paper reports the synthesis and characterization of a variety of functionally substituted alkyltropilidenes (7-alkylcycloheptatrienes). Of particular interest is the fact that electrophilic reagents in certain cases cause a fragmentation reaction which yields a tropylium (cycloheptatrienylium) ion and an aliphatic fragment which accounts for the alkyl substituent.

The unique stability of the tropylium ion^{1,2} suggested that it might serve as a leaving group in electrophilic substitution and elimination reactions. Some support for this supposition was found in the reported isolation of tropylium bromide from ditropyl ether,³ a reaction which may be considered an electrophilic displacement of a tropylium ion from oxygen by a proton. The quantitative conversion of tropyl isocyanate (or its homolog) to tropylium bromide (or its homolog) and cyanuric acid⁴ is formally a similar displacement on nitrogen. The isolation of N-tropylbenzamide from ditropylamine and benzoyl chloride^{3,5} could be the result of a displacement on nitrogen of the tropylium ion by the incipient benzoylium ion. The conversion of tropyl cyanide to tropylium salts under acid conditions⁴ serves as an example in which the tropylium ion leaves a carbon atom.

On the basis of these reports of electrophilic displacements of tropylium ion, it was anticipated that properly constituted functionally substituted 7-alkyltropilidenes might provide additional examples in which tropylium ion could serve as a positively charged leaving group in electrophilic processes. Accordingly, an investigation of the synthesis and reaction of a series of representative compounds was undertaken.

Entry to the desired alkyltropilidenes was gained through the nucleophilic attack of various active methylene compounds on the tropylium ion. The reaction occurs rapidly and conveniently in pyridine as solvent and hydrogen bromide acceptor

and gives good yields (46–83%) with the active methylene components used in spite of the use of crude tropylium bromide. The acetylacetone adduct is a solid; it was prepared from aqueous solution as well as from pyridine solution and appears to be a good derivative for isolating tropylium ion from aqueous solution. This type of condensation reaction was reported by Russian workers⁶ shortly after its use was begun independently in this work.

Some interest was attached to the question of the structure of the condensation products. Three possibilities were considered: (1) a C-alkylation product, (2) an O-alkylation product and (3) an ionic product in which an anion related to the active methylene component has replaced the bromide ion of tropylium bromide. This last possibility was immediately eliminated on the basis of the solubility in benzene and ether and the volatility of the products, the ultraviolet spectra (which were identical with those of tropilidene and its simple derivatives rather than those of tropylium salts) and the unexceptional reactions of the products.

That C-alkylation is the predominant course of the reaction is evident from the functionality of the product. Thus the adduct from acetylacetone gives a bis-2,4-dinitrophenylhydrazone and a di-oxime. The adduct from acetoacetic ester gives a mono-2,4-dinitrophenylhydrazone. None of these derivatives could be formed from reasonable O-alkylated adducts. The further transformations of these initial adducts offers incontrovertible evidence that C-alkylation occurs.

The possibility that ring contraction occurred⁷ during the condensation reaction to give substi-

(1) W. von E. Doering and L. H. Knox, *THIS JOURNAL*, **76**, 3203 (1954).

(2) H. J. Dauben, Jr., E. A. Gadecki, K. M. Harmon and D. L. Pearson, *ibid.*, **79**, 4557 (1957).

(3) W. von E. Doering and L. H. Knox, *ibid.*, **79**, 352 (1957).

(4) M. J. S. Dewar and R. Pettit, *J. Chem. Soc.*, 2021, 2026 (1956).

(5) W. von E. Doering and H. Krauch, *Angew. Chem.*, **68**, 661 (1956).

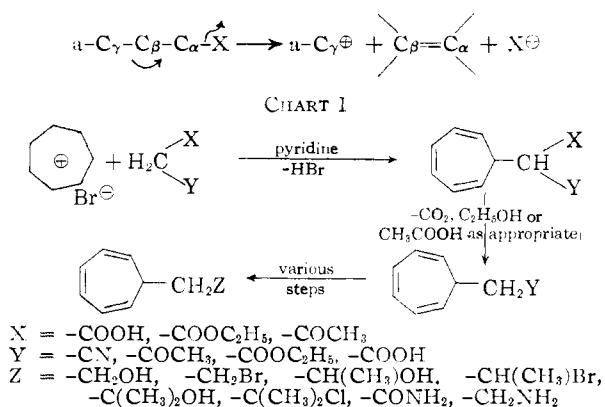
(6) M. E. Vol'pin, I. S. Akhrem and D. N. Kursanov, *Izvest. Akad. Nauk S.S.S.R., Otdel. Khim. Nauk*, 1501 (1957); *C. A.*, **62**, 7175c (1958).

(7) Ring contraction has been noted in oxidative processes on the tropylium ion⁴ and in certain reactions of substituted tropilidenes.^{4,5}

tuted alkylbenzenes is similarly ruled out by the ultraviolet spectra. In addition, the proton magnetic resonance spectra were taken in typical cases (the acetylacetone, the malonic ester, the acetic acid, the acetoacetic ester and the acetone derivatives) and found to be very complicated in the vinyl hydrogen region and very similar in this region to the spectrum exhibited by tropilidene⁸ itself. The fragmentation reactions, all of which produce tropylium ions, offer direct evidence of the integrity of the seven-membered ring in the condensation products.

Transformation of the initial condensation products to various other alkyl tropilidenes proceeded by standard methods including saponification, decarboxylation, esterification, Grignard synthesis, hydride reduction and replacement of hydroxyl by halogen. The presence of the tropilidene nucleus interferes with these reactions in no way; the yields are in the usual preparative range. In some cases it was preferable to perform two of these steps without isolation of the intermediate substance. The synthetic routes are summarized in Chart I. The tropilidene nucleus, on the other hand, was found to interfere with the action of nitrous acid on trotylalkyl amines.

Certain of these functionally substituted alkyl-tropilidenes react with electrophiles to give tropylium salts as the end product of a fragmentation reaction. Grob has discussed fragmentation reactions at some length.⁹ The reactions described in this paper fit into his general scheme, except that the tropylium ion ($\alpha\text{-C}_7^{\oplus}$) is stable as a cation and does not react further under the reaction conditions.

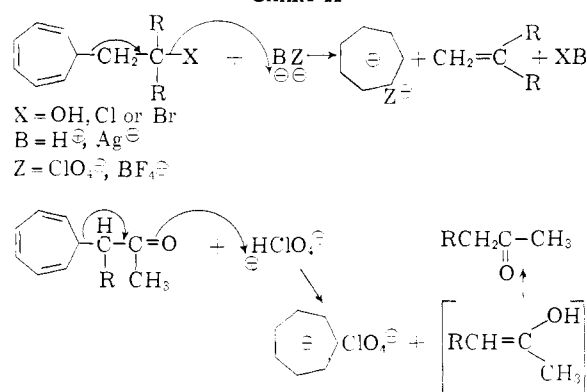


The fragmentation reactions reported here may be divided into two groups (see Chart II). In one, X is singly bonded to C_α and there results three fragments: free X, olefin and the tropylium ion. In the other, X is a carbonyl oxygen atom doubly bonded to C_α and only two fragments result: an enol and the tropylium ion. Both fragments have been isolated in at least one reaction typical of each group, and certain additional observations made. It is believed that this is the first example of an electrophilic fragmentation to a stable cation and an olefin; other examples may be anticipated in suitable systems. Fosse has reported fragmenta-

(8) W. von E. Doering, G. Laber, R. Vonderwahl, N. F. Chamberlain and R. B. Williams, *THIS JOURNAL*, **78**, 5448 (1958).

(9) C. A. Grob, *Experientia*, **13**, 126 (1957).

CHART II



tion to a stable cation and a carbonyl compound in the carbonyl substituted alkylxanthane series.¹⁰

A compound typical of the first group is 1-tropyl-2-methyl-2-propanol. When this substance in acetonitrile solution is treated with perchloric acid, a 67% yield of tropylium perchlorate can be isolated. The presence of isobutylene in the acetonitrile was shown by a vapor phase chromatogram. The corresponding secondary and primary alcohols (1-tropyl-2-propanol and 2-tropylethanol) did not give isolable quantities of tropylium perchlorate. No propylene could be detected in a distillate from the reaction of the secondary alcohol. The infrared spectra of the organic material recovered from the reaction mixtures indicated that aliphatic side chains were still present on the tropilidene nucleus although it was obvious that the material recovered was not pure starting material.

The tertiary chloride (1-tropyl-2-methyl-2-propyl chloride) gives tropylium perchlorate (51% isolated yield) and isobutylene (identified by vapor phase chromatography) on treatment with silver perchlorate in acetonitrile solution. The secondary bromide (1-tropyl-2-propyl bromide) gave no detectable quantities of propylene nor isolable quantities of tropylium perchlorate under the same conditions. Variations in the identity of the anion of the silver salt employed and in the solvent induced variations in the products identified. Silver nitrate in methanol gave isobutylene as well as a small amount of material tentatively identified as the methyl ether from the tertiary chloride. The same reagent gave a trace of propylene from the secondary bromide, the bulk of the material being accounted for as a mixture of nitrate ester and methyl ether. The primary bromide gave principally the nitrate ester. Use of silver tetrafluoroborate in benzene solution resulted in the isolation of a 23% yield of tropylium tetrafluoroborate from the tertiary chloride. No other products were isolated. The secondary bromide gave no isolable material under the same conditions.

In contrast to the good yields of certain fragmentation products from the tertiary alkyl derivatives reported above was the result obtained from the action of concentrated hydrochloric acid (containing ether to improve the solubility of the substrate) on 1-tropyl-2-methyl-2-propanol. This re-

(10) R. Fosse, *Bull. soc. chim. France*, [3] **35**, 1005 (1906); *Ann. chim. (Paris)*, [9] **13**, 154 (1920); R. Fosse and H. Robyn, *Compt. rend.*, **143**, 239 (1906).

action gave about 78% of non-fragmented products, predominately the chloride but probably also some olefin (by elimination), and 8% of tropylium ion, identified as its acetylacetone derivative.

There are two principal mechanisms by which these compounds might undergo fragmentation. One would involve a stepwise process in which alkyl carbonium ions are produced as discrete intermediates which may undergo fragmentation. The other would involve a process in which ionization is concerted with fragmentation.

It is apparent that, at least in the hydrochloric acid reaction, the concerted mechanism cannot be in force, for if it were the only product would be tropylium ion since loss of X would necessarily lead to fragmentation. On the other hand, all of the products observed can readily be understood on the basis of the intermediacy of a carbonium ion. In the hydrochloric acid reaction, the carbonium ion is formed and then partitioned: the major reaction occurs with the nucleophilic chloride ion to give chloride; minor amounts undergo olefin formation by loss of a tropylium ion (fragmentation) or a proton (normal elimination). In the reactions with perchloric acid or with silver salts in acetonitrile or methanol no such active nucleophile is present and the carbonium ion decomposes by the fragmentation path to a major extent, but can also react with solvent to a small extent. In the cases where the carbonium ion would be secondary, fragmentation is observed only to a very small extent in only one case. This is readily explicable on the basis of the idea that participation by solvent or anion on the backside of the carbon atom beta to the tropilidene nucleus is necessary to the loss of X so that substitution is preferred to fragmentation. The same is true to a greater extent in the case of the primary derivatives and explains the observation of the nitrate ester as the major product from the action of silver nitrate in methanol on the primary bromide.

The second main class of fragmentation reactions is that which employs carbonyl compounds as substrates. Under the influence of strong acids, tropanylacetylacetone and tropanylacetonone are cleanly converted to tropylium ion and the corresponding aliphatic ketones. Tropylium perchlorate (90 and 53%, respectively) was isolated in both cases and acetylacetone was isolated from the former reaction mixture as 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole. The reactions were investigated spectroscopically as well and the indications were that they are uncomplicated by any side reactions and give essentially quantitative yields.

It is clear from the ready formation of 2,4-dinitrophenylhydrazone derivatives of these carbonyl compounds under acid catalysis that the carbonyl oxygen can be protonated without inducing fragmentation reactions. However, it is not clear that these compounds can ever enolize without loss of tropylium. (Fragmentation here is merely an enolization where tropylium is lost instead of a proton.) Indeed, the fact that tropanylacetylacetone is slow to form a color with ferric chloride and that the color, once formed, appears to be the same as that formed with acetylacetone itself may be some indication that enolization prefers to occur

with tropylium loss in this series, just as silver ion-catalyzed dehalogenation prefers to occur with tropylium loss rather than proton loss.

Grob has observed that the reaction of the simple α -C-X systems occur uniformly more easily than the fragmentations of the α -C-C-C-X systems. This work supports his generalization. The tropanylethyl halides are stable covalent alkyl halides which, under sufficient provocation, can be induced to fragment. On the other hand, the simple tropanyl halides are completely unknown in the covalent state and apparently ionize spontaneously. The same parallel may be discerned in the alcohol series, in that tropanyl alcohol, despite intensive efforts, has never been isolated. The process corresponding to the fragmentation of tropanylacetonone is the protonation of tropone to form hydroxytropylium salts. The unusual basicity of tropone is well known.¹¹

We plan to undertake some kinetic experiments on selected fragmentation reactions in this series in the hope of clarifying the mechanistic processes involved.

Experimental

All ultraviolet spectra were taken in 95% ethanol solution on a Cary model 11 spectrophotometer unless otherwise noted. Routine infrared spectra were taken on a Perkin-Elmer model 21 on neat liquid samples. The few solid materials were examined either in chloroform solution or in potassium bromide disks. The two spectra done with lithium fluoride optics were determined on a Beckman IR4. Spectral determinations were made by Miss Donna Karasek. The microanalyses were done by Miss Heather King.

Melting points are corrected; boiling points are uncorrected.

The author is indebted to the Shell Chemical Co. for samples of bicycloheptadiene and tropilidene and for directions for the conversion of the former to the latter. Tropilidene was converted to tropylium bromide by the method of Doering and Knox.³ The material was used in the crude state as obtained after thorough washing with carbon tetrachloride, to avoid the large losses involved in purification.

Tropanylacetylacetone (Cycloheptatrienylacetylacetone).—To a stirred solution of 2.0 ml. (ca. 20 mmoles) of acetylacetone in 10 ml. of pyridine was added 2.00 g. (11.7 mmoles) of tropylium bromide. The mixture was warmed on the steam-bath for an hour and a half before being cooled and poured into 100 ml. of 1 N hydrochloric acid and 350 ml. of ether. The ether layer was dried and decolorized with activated charcoal. Petroleum ether (100 ml.) was added, and the mixture was concentrated to 80 ml. to give 1.85 g. (82%) of white needles, m.p. 123–125° on cooling. Recrystallization from petroleum ether raised the melting point to 124.7–125.2°; λ_{\max} 260 m μ (log ϵ 3.51), λ_{\min} 227 m μ (log ϵ 3.27).

Anal. Calcd. for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.98; H, 7.27.

The dioxime was prepared from 0.19 g. of the diketone and 0.28 g. of hydroxylamine hydrochloride in 2 ml. of pyridine and 2 ml. of absolute ethanol. After two hours at reflux, the solvent was removed and trituration with water induced crystallization. Repeated recrystallization from benzene-petroleum ether gave a low yield of cream colored crystals, m.p. 161.0–161.5.

Anal. Calcd. for $C_{12}H_{16}N_2O_2$: C, 65.43; H, 7.32. Found: C, 65.12; H, 7.29.

The *bis*-2,4-dinitrophenylhydrazone was prepared from an absolute ethanol solution of the reactants and a drop of concentrated hydrochloric acid. The product was recrystallized from ethyl acetate as fine yellow needles, m.p. 232–233° dec.

Anal. Calcd. for $C_{24}H_{22}N_4O_8$: C, 52.36; H, 4.03. Found: C, 52.24; H, 3.76.

(11) W. von E. Doering and F. L. Detert, *THIS JOURNAL*, **73**, 876 (1951); H. J. Dauben, Jr., and H. J. Ringold, *ibid.*, **73**, 876 (1951).

Tropylacetylacetonate; Derivatization of Aqueous Solutions of Tropylium Ion.—A solution of 2.23 g. (13 mmoles) of tropylium bromide in 10 ml. of distilled water was clarified by stirring with activated charcoal and filtration through Filter-cel. The resulting yellow solution was treated with 2.3 ml. (ca. 23 mmoles) of acetylacetonate. A white precipitate formed, but the yellow color was not entirely discharged. One ml. of pyridine was added dropwise with stirring. The yellow color was discharged as more white precipitate formed. The solid was collected and air-dried to give 1.70 g. (8.9 mmoles, 68%) of tropylacetylacetonate, m.p. 124–125°.

Ethyl Tropylacetylacetonate (Ethyl Cycloheptatrienylacetylacetonate).—A mixture of 2.00 ml. (15.6 mmoles) of ethyl acetylacetonate and 2.00 g. (11.7 mmoles) of tropylium bromide in 10 ml. of pyridine was stirred at room temperature overnight, warmed for an hour and a half on the steam-bath and poured into 140 ml. of 1 *N* hydrochloric acid. The reaction product was extracted with ether, decolorized with activated charcoal, dried with magnesium sulfate and finally distilled to give 2.14 g. (83%) of a viscous slightly yellow oil, b.p. 90–93° (0.3 mm.), n_{D}^{25} 1.5016, λ_{\max} 258 μ (log ϵ 3.49), λ_{\min} 228 μ (log ϵ 3.29).

Anal. Calcd. for $C_{13}H_{16}O_3$: C, 70.89; H, 7.32. Found: C, 70.99; H, 7.37.

The 2,4-dinitrophenylhydrazone was prepared by mixing solutions of 0.10 g. of the ketoester and 0.11 g. of 2,4-DNP in minimum amounts of absolute ethanol with one drop concentrated hydrochloric acid. After one hour at reflux, the mixture was cooled and the resulting crystals were thrice recrystallized from absolute alcohol to give yellow needles, m.p. 135.0–136.4°.

Anal. Calcd. for $C_{19}H_{20}N_4O_6$: C, 56.99; H, 5.04. Found: C, 57.02; H, 4.94.

Tropylacetone (Cycloheptatrienylacetone).—Solutions of 10.95 g. (49.7 mmoles) of ethyl tropylacetylacetonate in 50 ml. of alcohol and of 5.0 g. of potassium hydroxide in 20 ml. of water were combined and warmed for 45 minutes on the steam-bath; 10 ml. of concentrated hydrochloric acid was added cautiously. The potassium chloride was removed by filtration and the homogeneous filtrate concentrated until two layers formed. The oily phase was collected by extraction with four portions of ether, dried over magnesium sulfate, filtered, concentrated and distilled to give 5.44 g. (74%) of light yellow, mobile oil boiling at 77–84° (1.7–2.1 mm.). A portion was redistilled for analysis, b.p. 76° (1.8 mm.), n_{D}^{20} 1.5174, λ_{\max} 258 μ (log ϵ 3.57), λ_{\min} 228 μ (log ϵ 3.15).

Anal. Calcd. for $C_{10}H_{12}O$: C, 81.04; H, 8.16. Found: C, 81.20; H, 8.12.

The 2,4-dinitrophenylhydrazone was prepared as in the case of ethyl tropylacetylacetonate and recrystallized from ethanol-ethyl acetate to give orange needles, m.p. 170.0–171.0°.

Anal. Calcd. for $C_{16}H_{16}N_4O_4$: C, 58.53; H, 4.91. Found: C, 58.81; H, 5.06.

Tropylacetone could also be prepared (in 7% yield) by the direct action of tropylium bromide on a pyridine solution of acetone during 20 hours at room temperature. The melting point and mixture melting point of the 2,4-dinitrophenylhydrazone with that prepared by the method above was 169.0–171.0°.

A similar reaction between 1.00 ml. (11.2 mmoles) of 2-nitropropane and 1.00 g. (5.8 mmoles) of tropylium bromide in 5.0 ml. of pyridine resulted, after the customary workup, in 0.20 g. of a light yellow oil, b.p. ca. 95° (2.0 mm.). This was assumed to be 2-tropyl-2-nitropropane on the basis of its spectral properties [nitro group absorption at 1530–1550 and at 1350 cm^{-1} in the infrared and tropyl absorption in the ultraviolet: λ_{\max} 253.5 μ (log ϵ 3.59), λ_{\min} 228 μ (log ϵ 3.36)].

Tropylmalonic Acid (Cycloheptatrienylmalonic Acid).—To a solution of 2.50 ml. (16.5 mmoles) of diethyl malonate in 10 ml. of pyridine was added 2.00 g. (11.7 mmoles) of tropylium bromide. The mixture was heated on the steam-bath for two hours before it was worked up as in the case of ethyl tropylacetylacetonate to give 1.40 g. (48%) of a slightly viscous orange-yellow oil, b.p. 99–110° (0.3 mm.), λ_{\max} 257.5 μ (log ϵ 3.49), λ_{\min} 228 μ (log ϵ 3.18).

The diester was dissolved in 10 ml. of 95% ethanol and a solution of 1.1 g. of potassium hydroxide in 5 ml. of water was added. The mixture was heated on the steam-bath for

three hours. The basic mixture was extracted with ether to remove any non-acidic substances, acidified with about 25 ml. of 1 *N* hydrochloric acid and extracted with four 25-ml. portions of ether. The extracts were combined, dried over magnesium sulfate and concentrated. The residue was recrystallized from ether-petroleum ether to give 0.87 g. (80% from the ester) of colorless needles, m.p. 135–137° dec., λ_{\max} 258 μ (log ϵ 3.53), λ_{\min} 228 μ (log ϵ 3.15).

Anal. Calcd. for $C_{10}H_{10}O_4$: C, 61.85; H, 5.19. Found: C, 62.05; H, 4.99.

Tropylacetic Acid (Cycloheptatrienylacetic Acid) (By Decarboxylation).—A solution of 0.70 g. of tropylmalonic acid in 3 ml. of pyridine was heated on the steam-bath for an hour and a half. The cooled solution was poured into 50 ml. of 1 *N* hydrochloric acid and extracted with four 25-ml. portions of ether. The extracts were dried over magnesium sulfate, concentrated and distilled to give 0.32 g. (59%) of a white oil, b.p. ca. 106° (0.3–0.4 mm.). The *p*-bromophenacyl ester was prepared in the usual way to give white platelets, m.p. 85.5–86.5°.

Tropylacetic Acid (Direct Preparation).—To a stirred solution of 2.00 g. (19.2 mmoles) of malonic acid in 10 ml. of pyridine was added 2.00 g. (11.7 mmoles) of tropylium bromide. The temperature rose to about 45°. After 5 minutes, the mixture was put on the steam-bath and heated overnight. The cooled solution was poured into 150 ml. of 1 *N* hydrochloric acid and extracted with four 50-ml. portions of ether. The extracts were decolorized with activated charcoal, dried over magnesium sulfate, concentrated and distilled to give 1.44 g. (82%) of a viscous light yellow oil, b.p. 95–98° (0.3 mm.). The oil solidified on standing to hard colorless platelets, m.p. 30–33°, λ_{\max} 258 μ (log ϵ 3.56), λ_{\min} 225 μ (log ϵ 2.94).

Anal. Calcd. for $C_9H_{10}O_2$: C, 71.98; H, 6.71. Found: C, 72.07; H, 6.64.

The *p*-bromophenacyl ester was prepared in the usual way to give white platelets, m.p. and m.m.p. with that above 85.9–86.4°.

Anal. Calcd. for $C_{17}H_{15}BrO_2$: C, 58.80; H, 4.35. Found: C, 58.81; H, 4.07.

Tropylacetoneitrile (Cycloheptatrienylacetoneitrile).—To a stirred solution of 10.0 g. (133 mmoles) of cyanoacetic acid in 50 ml. of pyridine was added 10.0 g. (58.5 mmoles) of tropylium bromide. After a few minutes, 1.0 g. of copper bronze was added and the mixture heated to vigorous reflux for 19 hours. The mixture was poured into a solution of 60 ml. of concentrated hydrochloric acid in 200 ml. of water, and the resulting oily phase collected with three 75-ml. portions of ether. The extracts were washed with 5% sodium bicarbonate solution, dried, concentrated and distilled to give 3.41 g. (45%) of light yellow oil, b.p. 74–87° (0.8–0.6 mm.). This was redistilled and a center cut, an almost colorless, mobile oil, used for analysis, b.p. 80–84° (1.2 mm.) n_{D}^{25} 1.5331, λ_{\max} 258 μ (log ϵ 3.57), λ_{\min} 226 μ (log ϵ 3.10).

Anal. Calcd. for C_9H_9N : C, 82.41; H, 6.92; N, 10.68. Found: C, 82.61; H, 6.82; N, 10.77.

Tropylacetamide (Cycloheptatrienylacetamide).—A solution of 2.26 g. (15.0 mmoles) of tropylacetic acid in 25 ml. of benzene was treated with 3.1 ml. (ca. 43 mmoles) of thionyl chloride. The mixture was refluxed 1.5 hours before the bulk of the benzene and excess thionyl chloride was bailed off. More benzene was added and the solution saturated with gaseous ammonia. The mixture was poured into ether and concentrated aqueous ammonia. The layers were separated and the aqueous layer extracted once with chloroform. The combined organic layers were concentrated and the residue crystallized from benzene-hexane to give white platelets, m.p. 124–125.5°. A second crop was obtained from the mother liquor to give a total of 1.05 g. (47%). The analytical sample melted at 124–124.5°, λ_{\max} 258 μ (log ϵ 3.53), λ_{\min} 224 μ (log ϵ 2.95).

Anal. Calcd. for $C_9H_{11}NO$: C, 72.45; H, 7.43. Found: C, 72.39; H, 7.25.

2-Tropylethylamine (2-Cycloheptatrienylethylamine).—A solution of 4.29 g. (30.6 mmoles) of tropylacetoneitrile in 25 ml. of dry ether was added to an ice-cold slurry of 1.6 g. (42.3 mmoles) of lithium aluminum hydride in 150 ml. of dry ether. After four hours at room temperature, the excess hydride was decomposed by the careful addition of 3.2 ml. of

water followed by 2.4 ml. of 10% sodium hydroxide solution. After standing overnight, the mixture was filtered and the solid cake washed with fresh ether. The filtrate was dried with magnesium sulfate, filtered, concentrated and distilled to give 3.13 g. (76%) of colorless oil, darkening on standing, b.p. 78–82° (4 mm.), n_D^{20} 1.5340, λ_{\max} 258 μ ($\log \epsilon$ 3.49), λ_{\min} 225 μ ($\log \epsilon$ 2.91).

Identical material (superposable infrared spectra and n_D^{20} 1.5346) was obtained by a similar lithium aluminum hydride reduction of the tropylacetamide in 45% yield, 13% of the starting material being recovered. The route *via* the nitrile is clearly preferable for preparative purposes.

The benzamide was prepared from the amine and benzoyl chloride in pyridine and isolated by dilution with water. After four crystallizations from aqueous ethanol, the melting point of the white needles was 96.8–98.0°.

Anal. Calcd. for $C_{16}H_{17}NO$: C, 80.30; H, 7.16; N, 5.84. Found: C, 80.34; H, 7.14; N, 5.93.

Ethyl Tropylacetate (Ethyl Cycloheptatrienylacetate).—A mixture of 10.84 g. (72 mmoles) of propylacetic acid, 64 ml. of absolute ethanol, 32 ml. of toluene and two drops of concentrated sulfuric acid was heated under reflux one hour on the steam-bath. Then the condenser was set for distillation and the distillate was collected until it stopped collecting at a useful rate. The residue was taken up in ether and washed with 5% sodium bicarbonate solution. The ether layer was dried over magnesium sulfate, filtered, concentrated and distilled to give 10.58 g. (82%) of a colorless mobile oil, b.p. 95–97° (3.8 mm.), n_D^{25} 1.4996, λ_{\max} 258 μ ($\log \epsilon$ 3.49), λ_{\min} 226 μ ($\log \epsilon$ 2.99).

Anal. Calcd. for $C_{11}H_{14}O_2$: C, 74.13; H, 7.92. Found: C, 73.91; H, 8.09.

2-Tropylethanol (2-Cycloheptatrienylethanol).—A solution of 3.53 g. (19.8 mmoles) of ethyl tropylacetate in 50 ml. of anhydrous ether was added slowly to a slurry of 1.0 g. of lithium aluminum hydride (26.4 mmoles) in 100 ml. of anhydrous ether. The mixture was stirred at room temperature for an hour and a half before the excess reagent was destroyed by the cautious addition of 2.0 ml. of water followed by 1.6 ml. of 10% sodium hydroxide solution. After standing overnight the mixture was filtered and the filter cake washed with ether. The ether filtrates were dried over magnesium sulfate, filtered, concentrated and distilled to give 2.38 g. (88%) of a colorless oil with a dank earthy odor, b.p. 91–95° (2.8 mm.), n_D^{25} 1.5360.

Anal. Calcd. for $C_9H_{12}O$: C, 79.37; H, 8.88. Found: C, 79.56; H, 8.91.

A similar yield of reduction product is obtained by the action of lithium aluminum hydride directly on propylacetic acid.

The 3,5-dinitrobenzoate was prepared from 194.6 mg. of 3,5-dinitrobenzoic acid, 348.9 mg. of *p*-toluenesulfonyl chloride and 124.3 mg. of 2-tropylethanol by the method of Brewster and Ciotti.¹² The ester was isolated by ether extraction and purified by three crystallizations from 95% ethanol to yield yellow needles, m.p. 79.5–80.5°.

Anal. Calcd. for $C_{16}H_{14}N_2O_6$: C, 58.18; H, 4.27. Found: C, 58.42; H, 4.50.

1-Tropyl-2-propanol (1-Cycloheptatrienyl-2-propanol).—To a stirred solution of 4.77 g. (32.2 mmoles) of propylacetone in 50 ml. of methanol at 0° was added 1.20 g. (32.4 mmoles) of sodium borohydride. After one hour, the solution was poured into 300 ml. of water and extracted with five 20-ml. portions of chloroform. The extracts were dried over magnesium sulfate, filtered, concentrated and distilled to give 4.02 g. (83%) of colorless oil, b.p. 92–95° (2.3 mm.), n_D^{20} 1.5242, λ_{\max} 259 μ ($\log \epsilon$ 3.51), λ_{\min} 225 μ ($\log \epsilon$ 2.85).

Anal. Calcd. for $C_{10}H_{14}O$: C, 79.95; H, 9.39. Found: C, 80.24; H, 9.24.

The 3,5-dinitrobenzoate was formed as in the case of the corresponding primary alcohol and was crystallized from 95% ethanol in the form of yellow prisms, m.p. 101–102°.

Anal. Calcd. for $C_{17}H_{16}N_2O_6$: C, 59.30; H, 4.69. Found: C, 59.58; H, 4.84.

1-Tropyl-2-methyl-2-propanol (1-Cycloheptatrienyl-2-methyl-2-propanol).—A solution of 3.56 g. (20.0 mmoles) of

ethyl tropylacetate in 20 ml. of dry ether was added to a solution of methylmagnesium iodide prepared from 1.46 g. (60 mmoles) of magnesium turnings, 3.73 ml. (*ca.* 60 mmoles) of methyl iodide and 75 ml. of dry ether. The mixture was stirred for two hours at room temperature before it was poured into a mixture of 10 g. of ammonium chloride, 20 ml. of water and 80 g. of ice. The aqueous solution was extracted with several portions of ether and the combined ether layers were dried over magnesium sulfate, filtered, concentrated and distilled to give 2.62 g. (80%) of a colorless oil, b.p. 89–93° (3.1–2.9 mm.). A redistilled portion, b.p. 84–85° (2.0 mm.), n_D^{20} 1.5178, was analyzed, λ_{\max} 257 μ ($\log \epsilon$ 3.53), λ_{\min} 223 μ ($\log \epsilon$ 2.92).

Anal. Calcd. for $C_{11}H_{16}O$: C, 80.44; H, 9.83. Found: C, 80.69; H, 9.87.

The phenylurethan was prepared by heating equal volumes of the alcohol and phenyl isocyanate with a drop of pyridine for 10 minutes. The cooled mixture was taken up in carbon tetrachloride and filtered to remove diphenylurea. The filtrate was diluted with hot petroleum ether (60–80°) and filtered to remove additional diphenylurea. The filtrate was concentrated and cooled to give needles which were recrystallized from petroleum ether. The colorless needles were dried at 0.1 mm. at 78° and melted at 105.5–106°.

Anal. Calcd. for $C_{18}H_{21}NO_2$: C, 76.29; H, 7.47. Found: C, 76.06; H, 7.28.

1-Tropyl-2-methyl-2-propyl Chloride (1-Cycloheptatrienyl-2-methyl-2-propyl Chloride).—A mixture of 50 ml. of concentrated hydrochloric acid and 20 ml. of ether in a 250-ml. separatory funnel was cooled under the tap. 1-Tropyl-2-methyl-2-propanol, 4.53 g. (27.6 mmoles), was added and the mixture shaken vigorously by hand for 10 minutes. The mixture was diluted with 100 ml. of water and extracted with three 25-ml. portions of ether. The extracts were combined, dried over magnesium sulfate, filtered, concentrated and distilled. A total of 3.96 g. (*ca.* 78%) of colorless oil was collected at 71–80° (*ca.* 1 mm.), n_D^{20} 1.5140. The infrared spectrum indicated small amounts of alcohol (ν_{\max} 3420, 3520) and terminal methylene (ν_{\max} 905) impurities. These were removed by renewed treatment with concentrated hydrochloric acid and redistillation. The analytical sample, b.p. 79–81° (2.6 mm.), n_D^{20} 1.5183, showed no absorption at the above-mentioned frequencies, λ_{\max} 256 μ ($\log \epsilon$ 3.52), λ_{\min} 224 μ ($\log \epsilon$ 3.02). A sample in acetonitrile solution was observed spectroscopically before and after 20 hours at reflux. No change in λ_{\max} or ϵ was observed, indicating that no spontaneous ionization and fragmentation occurred.

Anal. Calcd. for $C_{11}H_{16}Cl$: C, 72.31; H, 8.28. Found: C, 72.57; H, 8.44.

The aqueous layer left after the ether extraction of the chloride was treated with 5 ml. of acetylacetone and cautiously basified with potassium carbonate. Near neutrality, the color changed abruptly from light yellow to light orange and a white precipitate formed. The solid was collected and found to be propylacetylacetone, m.p. 123–124°, 0.43 g. (8%).

1-Tropyl-2-propyl Bromide (1-Cycloheptatrienyl-2-propyl Bromide).—A mixture of 1.72 g. (11.45 mmoles) of 1-tropyl-2-propanol, 2.3 ml. of benzene, 0.55 ml. of pyridine and 0.39 ml. (*ca.* 12.7 meq.) of phosphorus tribromide was prepared in an ice-bath and then allowed to warm to room temperature with continuous stirring overnight. The mixture was transferred to a small distillation flask and the benzene removed at 60 mm. up to a bath temperature of 90°. The pressure was then reduced to 1.2 mm. and the residual yellow solid gradually decomposed at a bath temperature of 140–165°. White sublimate was largely decomposed to additional liquid products by application of the free flame to the exposed portions of the distillation apparatus. The distillate contained traces of solid material. Redistillation removed this and gave 1.73 g. (8.1 mmoles, 71%) of colorless oil, b.p. 80–82.5° (0.6–0.7 mm.), n_D^{20} 1.5430.

Anal. Calcd. for $C_{10}H_{14}Br$: C, 56.34; H, 6.15. Found: C, 57.80; H, 6.19.

Redistillation gave material which afforded an even poorer analysis. The reason for the poor analysis is unknown.

2-Tropylethyl Bromide (2-Cycloheptatrienylethyl Bromide).—A mixture of 1.02 g. (7.46 mmoles) of 2-tropylethanol and 0.4 ml. (*ca.* 12.6 equiv.) of phosphorus tribromide in 20 ml. of anhydrous ether was kept in the refrigerator for

(12) J. H. Brewster and C. J. Ciotti, Jr., *THIS JOURNAL*, **77**, 6214 (1955).

five days. It was then poured into a mixture of 25 ml. of 10% sodium carbonate solution and 25 ml. of 5% sodium bicarbonate solution and the resulting mixture was steam distilled until no more oily layer collected. The ethereal layer was separated, dried over magnesium sulfate, filtered, concentrated and distilled. A colorless oil, 0.59 g., was collected at 4–4.5 mm. at 86–87°. The material was obviously contaminated with unreacted alcohol (ν_{\max} 3560 and 3400). No attempt was made to obtain an analysis. More satisfactory material might be obtained by the procedure used above for 1-tropyl-2-propyl bromide.

Fragmentation of 1-Tropyl-2-methyl-2-propanol.—To a solution of 0.09 g. (0.55 mmole) of the carbinol in 10 ml. of dried acetonitrile was added 0.12 ml. (1.45 mmoles) of 70% perchloric acid. The solution turned to a light red-orange color. After five minutes at room temperature, the mixture was concentrated *in vacuo* to about 1 ml. Ethyl acetate was added to the residue and the mixture concentrated again to about 5 ml. The white crystals (0.07 g., ca. 67%) in the concentrate were collected and found to explode in a melting point tube near 280°. The infrared spectrum was identical with a sample of tropylium perchlorate prepared by the addition of perchloric acid to an acetic acid solution of tropylium bromide (principal ν_{\max}^{Br} 3025, 1475, 665 and 1025–1125 cm^{-1}) (compare the spectrum of tropylium bromide¹³).

In another experiment, the reaction mixture was distilled after five minutes at room temperature into a Dry Ice cooled container until about four drops of distillate had collected. The distillate warmed to 0° was subjected to vapor phase chromatography at 59° on a three meter carbowax column. A peak was observed with an identical elution time as that observed with authentic isobutylene.

Attempted Fragmentation of 1-Tropyl-2-propanol.—To a solution of 0.13 g. (0.87 mmole) of the alcohol in 6 ml. of dried acetonitrile was added 0.12 ml. (ca. 1.45 mmoles) of 70% perchloric acid. The mixture was warmed with a microburner, the vapors being led to a Dry Ice cooled receiver which contained 0.5 ml. of pentane to dissolve any evolved propylene. After a few minutes at gentle reflux, a drop or two of acetonitrile was distilled over. The pentane solution, kept at Dry Ice temperature, was subjected to vapor phase chromatography.¹³ No propylene could be detected in the pentane.

The residue was concentrated *in vacuo*, ethyl acetate was added and the mixture concentrated further. No solid formed (therefore, essentially no tropylium perchlorate had formed). The solution was taken to dryness and the residue dissolved in chloroform for an infrared spectrum. The material was obviously very impure and contained very little starting material. There was no O–H absorption, but there were moderately strong bands in the carbonyl region, at 1660 and 1710 cm^{-1} . Poorly resolved bands at ca. 2860, 2920, 1450 and 1465 cm^{-1} indicated that the side chain was still present, *i.e.*, that no fragmentation had occurred. No further attempts were made to characterize the products of this reaction.

An analogous experiment with 2-tropylethanol was performed except that a bicarbonate wash of an ethereal solution of the residue from the ethyl acetate concentration was included to remove perchloric acid. Again no tropylium perchlorate was observed from the ethyl acetate solution and the infrared spectrum of the ultimate chloroform solution of the organic products showed retention of aliphatic C–H bands, appearance of strong carbonyl absorption and a large loss of intensity of the O–H absorption band.

Silver Perchlorate Fragmentation of 1-Tropyl-2-methyl-2-propyl Chloride.—To a solution of 212.8 mg. (1.03 mmoles) of silver perchlorate in 10 ml. of acetonitrile was added 186.1 mg. (1.02 mmoles) of the tertiary chloride. Silver chloride precipitated rather slowly as the mixture was heated. The vapors were led to 0.5 ml. of pentane cooled in Dry Ice. The pentane solution was shown to contain isobutylene by vapor phase chromatography comparison with an authentic sample.¹³ The residue from the distillation was filtered to remove silver chloride and the silver chloride was washed with hot ethanol. The filtrate was concentrated *in vacuo*, the residue taken up in ethyl acetate and boiled briefly to dissolve the colored impurities from the solid. The crystals, collected by filtration and washed with fresh ethyl acetate,

amounted to 98.7 mg. (0.52 mmole, 51%) of tropylium perchlorate.

In an identical experiment with 1-tropyl-2-propyl bromide there was no evidence of propylene in the vapor phase chromatogram and a considerable portion of the starting material was re-isolated from the reaction mixture.

Silver Nitrate Fragmentation of 1-Tropyl-2-methyl-2-propyl Chloride.—To a solution of 147.2 mg. (0.866 mmole) of silver nitrate in 5 ml. of methanol was added 154.8 mg. (0.847 mmole) of the tertiary chloride. There was an immediate formation of a dense white precipitate of silver chloride. The mixture was distilled into a Dry Ice cooled receiver until about six drops of methanol had collected. The distillate was subjected to vapor phase chromatography (at 59° on the three meter carbowax column) and found to contain isobutylene.

The residue from the distillation was treated with 0.5 ml. of acetylacetone and basified slowly with ammonia. Excess ammonia was added and the mixture extracted with ether, dried over magnesium sulfate and concentrated. The residue was dissolved in pentane and chromatographed on alumina. The pentane eluates gave an oil whose infrared spectrum (in chloroform) indicated no functional groups except an ether linkage (1070 cm^{-1}) and retention of the tropyliene nucleus (669, 1685, 1770, 1880, 1930 cm^{-1}) and the geminal dimethyl group of the alkyl side-chain (1364 and 1378 cm^{-1}). The oil, on this basis, is formulated as methyl 1-tropyl-2-methyl-2-propyl ether. No tropyliacetone could be isolated from the further eluates from the column.

Silver Nitrate Fragmentation of 1-Tropyl-2-propyl Bromide.—To a solution of 176.1 mg. (1.037 mmoles) of silver nitrate in 5 ml. of methanol was added 199.5 mg. (0.937 mmole) of the bromide. Formation of silver bromide began at room temperature, but was forced to completion by warming the reaction vessel, the vapors being led to a Dry Ice cooled receiver which contained 1.00 ml. of pentane. The pentane solution was analyzed by vapor phase chromatography¹³ and found to contain traces of propylene. No effort was made to isolate the tropylium fragment.

The residue from the distillation of the propylene was shaken with ether and concentrated aqueous ammonia. The ether layer was washed with water, dried over magnesium sulfate, filtered, concentrated and its infrared spectrum taken. Strong absorption occurred at 1275 and 1625 cm^{-1} , indicating that a major portion of the reaction yielded the covalent nitrate ester, 1-tropyl-2-propyl nitrate.

A similar experiment, using the impure 2-tropylethyl bromide gave rise to nitrate ester also, as indicated by absorption at 1630 and 1280 cm^{-1} in the infrared region. It was contaminated with alcohol, presumably the one which contaminated the starting material.

Silver Tetrafluoroborate Fragmentation of 1-Tropyl-2-methyl-2-propyl Chloride.—A suspension of 118.8 mg. (ca. 0.5 mmole) of commercial, undried silver oxide in 25 ml. of toluene was treated with boron trifluoride.¹⁴ The silver oxide rapidly dissolved, leaving a small amount of immiscible liquid. To this mixture was added 179.8 mg. (0.984 mmole) of 1-tropyl-2-methyl-2-propyl chloride. The reaction mixture became red and precipitated an off-white solid. After 10 minutes, the reaction mixture was treated with dry ether and filtered. The solid was boiled in absolute ethanol and filtered again while hot. The light amber filtrate was cooled in ice to give white crystals which were collected and washed with ether. They amounted to 40.3 mg. (23%) and melted with decomposition from 225° (lit.⁴ m.p. 242° dec.). The infrared spectrum confirmed their identity as tropylium tetrafluoroborate, since absorption maxima occurred at 640, 665, 1478, 2975 and 3020 cm^{-1} (tropylium ion) and between 1025 and 1125 cm^{-1} (BF_4 ion). No attempt was made to isolate other materials from the reaction mixture, since it was obvious that extensive decomposition had occurred.

An analogous experiment with 1-tropyl-2-propyl bromide gave no isolable quantity of tropylium tetrafluoroborate. No starting material could be reisolated from the reaction mixture.

Fragmentation of Tropyliacetone.—A solution of 127.8 mg. (0.67 mmole) of tropyliacetone in 5.0 ml. of glacial acetic acid was treated with 0.1 ml. (ca. 1.4 mmoles) of 70% perchloric acid. A white precipitate formed im-

(13) The author is indebted to Mr. Robert Wilcox for his assistance and for the use of his 20 foot dimethyl sulfolane on brick dust column.

(14) Cf. H. Meerwein and R. Wunderlich, *Angew. Chem.*, **69**, 481 (1957); H. Meerwein, *et al.*, *Arch. Pharm.*, **291**, 541 (1958).

mediately and was collected on a sintered glass funnel and washed with acetic acid and anhydrous ether. The tropylium perchlorate (infrared spectrum identical with authentic material) collected in this way amounted to 115.4 mg. (90%). The filtrate and acetic acid wash was added to a solution of 129.6 mg. (0.655 mmole) of 2,4-dinitrophenylhydrazine in glacial acetic acid. The solution lightened in color while standing overnight. The 1-(2,4-dinitrophenyl)-3,5-dimethylpyrazole was isolated by dilution with a large volume of water. After recrystallization from aqueous ethanol it amounted to 128.9 mg. (73%), m.p. and m.m.p. with authentic material prepared from acetylacetone, 122.5–123.0°.

Fragmentation of Tropanylacetone.—A solution of 140.0 mg. (0.945 mmole) of tropanylacetone in 5.0 ml. of glacial acetic acid was treated with 0.15 ml. (ca. 1.8 mmoles) of 70% perchloric acid. The first appearance of crystals occurred in about 12 minutes. After three hours, 107.9 mg. (53.5%) of tropylium perchlorate was collected by filtration. The filtrate was mixed with 2,4-dinitrophenylhydrazine solution, but no acetone 2,4-dinitrophenylhydrazone was isolated.

The fragmentation reactions of tropanylacetone and of tropylium were also conducted in dilute solution in acetonitrile and the products detected spectroscopically. A solution of tropanylacetone ($6.51 \times 10^{-4} M$) in acetonitrile showed essentially unchanged absorption from that shown in ethanol. Perchloric acid was added to a concentration of $6.23 \times 10^{-3} M$ and the resulting mixture diluted 10:1. The spectrum now observed was, within experimental error, that calculated for an equimolar solution of tropylium perchlorate (λ_{\max} 275 $m\mu$, $\log \epsilon$ 3.64; λ_{infl} 268.5 and 280.5 $m\mu$, $\log \epsilon$ 3.52 and 3.60; λ_{\min} 245 $m\mu$, $\log \epsilon$ 2.57) and acetylacetone (λ_{\max} 273 $m\mu$, $\log \epsilon$ 3.82) in perchloric acid solution. Spectra of a solution $5.40 \times 10^{-4} M$ in tropanylacetone and $1.05 \times 10^{-3} M$ in perchloric acid changed with time; spectra taken within 10 minutes showed only partial loss of tropanyl absorption and partial appearance of tropylium absorption; after an hour the spectrum had the appearance of that of pure tropylium ion, though the extinction coefficients had not yet attained the proper magnitude. The series of spectra exhibited three isosbestic points, at 239 $m\mu$ ($\log \epsilon$ 3.30), 267 $m\mu$ ($\log \epsilon$ 3.48) and ca. 289 $m\mu$ ($\log \epsilon$ ca. 3.06), indicating that the reaction involved only two light absorbing species, the tropylium ion and tropanylacetone.¹⁵

Tropanylacetone and Ferric Chloride Solution.—Tropanylacetone slowly develops a wine-red color with alcoholic ferric chloride. Spectrophotometric comparison of the colors was made imprecise by the interfering color of the ferric chloride itself. Difference curves between the spectra of the ferric chloride solution and the tropanylacetone-ferric chloride mixture gave a maximum at $495 \pm 20 m\mu$.

(15) W. West in Weissberger's "Technique of Organic Chemistry," Vol. IX, Interscience Publishers, Inc., New York, N. Y. 1956, p. 68.

A similar procedure with acetylacetone gave a maximum at $490 \pm 15 m\mu$. Absorption of the species in solution was too strong to be able to detect absorption due to the seven-membered ring species in the ultraviolet. It was not possible, then, to obtain proof that tropylium loss accompanied enolization, but on the assumption that tropanylacetone enolate-ferric chloride complex would absorb at a significantly different wave length from acetylacetone enolate-ferric chloride complex itself, the coincidence of maxima is indicative of tropylium loss.

Base-induced retro-Claisen Reaction of Tropanylacetone.—A few milligrams of tropanylacetone was shaken vigorously with 10% sodium hydroxide solution. The solid slowly dissolved and gave rise to an oily suspension. Some 95% ethanol was added to increase mutual solubility and the mixture shaken some more. The mixture was acidified with concentrated sulfuric acid and poured into an ethanol solution of 2,4-dinitrophenylhydrazine. The yellow precipitate which formed almost immediately was collected and recrystallized from ethanol-ethyl acetate, m.p. and m.m.p. with the tropanylacetone 2,4-dinitrophenylhydrazone described above, 171–172°.

Infrared Spectra.—Infrared spectra of the compounds reported here and a few other tropilidene derivatives already in the literature were taken during the course of this investigation. Certain bands were found to be characteristic of the tropilidene nucleus.

Strong bands appeared in the 685–705 and the 735–755 cm^{-1} regions in the twenty-two cases examined. Another band, always sharp, usually strong, but sometimes only medium in intensity, could be observed in the 1358–1410 cm^{-1} region in all these cases. Ditropyl shows weak bands at 1688, 1771, 1880 and 1935 cm^{-1} . Bands in these general regions (1685–1694, 1740–1777, 1850–1895 and 1905–1940 cm^{-1} , respectively) were exhibited by the majority of the compounds investigated, though in several cases these absorptions were obscured by neighboring strong absorptions due to carbonyl groups or were too weak to detect under the conditions used. Benzenoid compounds show similar weak absorption in this region. The tropilidene derivatives, however, do not absorb characteristically near 1500 and 1600 cm^{-1} and so can be readily distinguished from benzene derivatives.

Ditropyl,³ ditropyl ether,¹ tropanyl methyl ether¹ and tropanyl cyclopentadiene⁵ showed absorption near 2800 cm^{-1} , probably due to the C–H stretching frequency of the hydrogen on the saturated carbon of the tropilidene nucleus. This band is obscured by other C–H stretching bands under ordinary conditions in the other compounds, but it can be detected by use of lithium fluoride optics as was done in the case of ethyl tropanylacetate and 1-tropanyl-2-methyl-2-propanol which showed this absorption near 2760 cm^{-1} .

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[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY, UNIVERSITY OF NEW SOUTH WALES]

Glycol Fission in Rigid Systems. I. The Camphane-2,3-diols¹

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The four diastereomeric camphane-2,3-diols—all having the skeletal configuration of (+)-camphor—have been prepared. Hydrogenation of camphorquinone gave mainly the 2-*exo*,3-*exo*-isomer; the 2-*exo*,3-*endo*-diol was obtained from 3-*endo*-hydroxycamphor, and the 2-*endo*,3-*exo*-diol from 2-*endo*-hydroxyepicamphor, by hydrogenation; in both cases camphane-2-*endo*,3-*endo*-diol is also formed.

The *cis*-diols react very rapidly, the *trans*-diols very slowly, with lead tetraacetate, phenyl iodosoacetate and periodic acid, indicating the importance of the relative positions of the oxygen atoms in glycol fission.

Dimler and his co-workers^{2,3} have shown that 1,6-anhydro- β -D-glucofuranose and 1,6-anhydro- α -D-galactofuranose are resistant to the action of

(1) Presented before the Division of Organic Chemistry, 132nd National A.C.S. Meeting, New York, N. Y., September 11, 1957. Abstracted from part of the Ph.D. thesis of R. J. Young, Sydney, 1958.

(2) R. J. Dimler, H. A. Davis and G. E. Hübner, *THIS JOURNAL*, **68**, 1377 (1946).

(3) B. H. Alexander, R. J. Dimler and C. L. Mehlretter, *ibid.*, **73**, 4658 (1951).

sodium metaperiodate, periodic acid and lead tetraacetate although each compound contains a vicinal glycol group. The fact that the two hydroxyl groups are *trans*-situated in five-membered rings does not, in itself, explain the non-occurrence of the usual glycol fission since *trans*-cyclopentane-1,2-diol⁴ and L-threitol⁵ (*trans*-tetrahydrofuran-3,4-diol) react under these circum-

(4) (a) R. Criegee, E. Buchner and W. Walther, *Ber.*, **73**, 571 (1940); (b) V. C. Bulgrin, *J. Phys. Chem.*, **61**, 702 (1957).

(5) H. Klosterman and F. Smith, *THIS JOURNAL*, **74**, 5336 (1952).