[CONTRIBUTION FROM THE CONVERSE MEMORIAL LABORATORY OF HARVARD UNIVERSITY]

Triptycene 1-Carboxylic Acid and Related Compounds. The Decomposition of Ditriptoyl Peroxide

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Triptycene-1-carboxylic acid (9,10-*o*-benzenoanthracene-9-carboxylic acid) has been prepared and with it a number of other triptycene derivatives. The acyl peroxide prepared from this acid decomposes in benzene at 80° somewhat faster than benzoyl peroxide. The readiness of formation of the triptycyl free radical under these conditions is indicated by the appearance of about 40% of triptycene among the products, which is supplanted by a like amount of 1-iodotriptycene when the decomposition is conducted in the presence of iodine. The ability of the triptycyl radical to capture a hydrogen atom from benzene indicates that, as would be expected from previous observations, the stability which characterizes the triphenylmethyl radical is totally lacking in the triptycyl radical. A product results to the extent of about 16% which is believed to arise from a carboxyl inversion reaction like that of Leffler[17] which is a polar rearrangement proceeding concurrently with the free radical decomposition. 1-Iodotriptycene, obtainable from the decomposition of the peroxide, appears to be totally inert to displacement reactions in boiling ethyl alcohol as had previously been observed for 1-bromotriptycene. Taken in conjunction with recent results of Doering and of Roberts, this indicates that benzene rings fused on the bridges of bicyclo-[2,2,2]octane have a strongly deactivating influence upon the carbon–bromine bond at position 1, which may be due in part to an electronegative inductive effect and, in part, to a stiffening of the internal bond angles of the cage ring system.[2]

Introduction

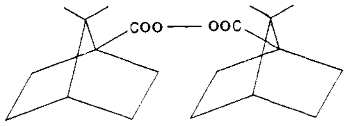
Derivatives of bicyclo[2,2,1]heptane and of bicyclo[2,2,2]octane having substituents at the bridgehead (C_1) have been of interest in connection with the formation of carbonium ions, carbanions and free radicals. Results to date have indicated that the difficulty of forming a bridgehead carbonium ion from the corresponding alcohol or halide increases in the order: bicyclo[4,3,1]decane,[3] bicyclo[2,2,2]octane,[4] bicyclo[2,2,1]heptane.[5a,5b]

The reaction of nitrous acid with amines, recognized as a method of more than adequate vigor to produce the most unstable acyclic carbonium ions,[6a,6b] proceeds readily with 1-aminoapocamphane,[7] and it is not established to what extent this represents the forcible formation of a carbonium ion, or whether a significantly different explanation resides in its formal resemblance to the $S_{N}i$ reaction.[8]

The most common methods of producing aliphatic free radicals, the thermal or photochemical decomposition of diacyl peroxides or azo compounds, are analogous to the last-named method for the production of carbonium ions in that they suffice for the generation of aliphatic free radicals with no stabilizing structural features. It is noted, however, that free radicals such as benzyl, *t*-butyl, or trichloromethyl, with any stability above that of simple alkyls, are produced from the related diacyl peroxides at strikingly lower temperatures than those at which benzoyl and acetyl peroxides decompose. Such accelerated decomposition is probably a criterion for the occurrence of the oft-postulated concerted decomposition of an acyl peroxide into carbon dioxide, a carboxylate free radical, and an alkyl radical[10]

$$\text{RCOO—OOCR} \longrightarrow \text{R}\cdot + \text{CO}_2 + \text{RCOO}\cdot$$

especially since such concerted decomposition has been shown not to be general for benzoyl peroxides acting as polymerization initiators.[11] The examination of the products[12] and kinetics[13] of decomposition of diapocamphoyl peroxide (I) has yielded no evidence that this method encounters any difficulty in generating a free radical with its odd electron on the bridgehead of a bicyclo-[2,2,1]heptane ring. The reactions of 1-halobicyclo[2,2,1]heptanes with metals, however, indicate a degree of reluctance to form free radicals readily detectable by this less vigorous method, though this reluctance is definitely less in amount than in the case of carbonium ion formation.



I

Triptycene and its 1-substitution products (II) contain the bicyclo[2,2,2]octane ring system and might, at first sight, be expected to be closer to this parent substance in the matter of strain than to bicyclo[2,2,1]heptane. This, however, is not the case, since the strainless ring of bicyclo[2,2,2]-

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(1) Standard Brands Fellow, 1951–1952.

(2) For previous papers on triptycene and its derivatives see (a) P. D. Bartlett, M. J. Ryan and S. G. Cohen, THIS JOURNAL, **64**, 2649 (1942); (b) P. D. Bartlett, S. G. Cohen, J. D. Cotman, Jr., N. Kornblum, J. R. Landry and E. S. Lewis, *ibid.*, **72**, 1003 (1950); (c) P. D. Bartlett and E. S. Lewis, *ibid.*, **72**, 1005 (1950).

(3) D. H. R. Barton, T. Bruun and A. S. Lindsey, *J. Chem. Soc.*, 2210 (1952).

(4) J. D. Roberts, W. T. Moreland, Jr., and W. Frazer, THIS JOURNAL, **75**, 637 (1953).

(5) (a) W. von E. Doering and E. F. Schoenwaldt, *ibid.*, **73**, 2333 (1951); (b) W. von E. Doering, M. Levitz, A. Sayigh, M. Sprecher and W. P. Whelan, Jr., *ibid.*, **75**, 1008 (1953).

(6) (a) J. D. Roberts and R. H. Mazur, *ibid.*, **73**, 2513 (1951); (b) W. A. Waters, *J. Chem. Soc.*, 266 (1942).

(7) P. D. Bartlett and L. H. Knox, THIS JOURNAL, **61**, 3184 (1939).

(8) The observations in connection with internal return (W. G. Young, S. Winstein and H. L. Goering, *ibid.*, **73**, 1958 (1951); S. Winstein and D. Trifan, *ibid.*, **74**, 1154 (1952); S. Winstein and K. C. Schreiber, *ibid.*, **74**, 2165 (1952)), show that free competition with outside ionic reagents is not a necessary mark of an ionization mechanism. Both ionic and free radical (M. S. Matheson, *J. Chem. Phys.*, **13**, 584 (1945)) processes are now known in which reaction between dissociation products of a single molecule takes precedence over their involvement with other reagents. The known examples of the $S_{N}i$ may fall within this class.[9]

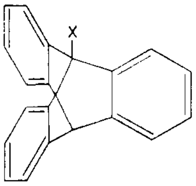
(9) W. A. Cowdrey, C. D. Hughes, C. K. Ingold, S. Masterman and A. D. Scott, *J. Chem. Soc.*, 1267 (1937).

(10) M. S. Kharasch and M. T. Gladstone, THIS JOURNAL, **65**, 16 (1943); D. H. Hey and W. A. Waters, *Chem. Revs.*, **21**, 169 (1937).

(11) P. D. Bartlett and S. G. Cohen, THIS JOURNAL, **65**, 543 (1943); G. S. Hammond, *ibid.*, **72**, 3737; G. S. Hammond and L. M. Soffer, *ibid.*, **72**, 4711 (1950).

(12) M. S. Kharasch, F. Englemann and W. H. Urry, *ibid.*, **65**, 2428 (1943).

(13) W. F. Sager, Thesis, Harvard University, 1948.



II

octane can have its 12 internal bond angles all equal to the tetrahedral value of 109°28′, while the benzene rings of triptycene call for internal angles of 120° for the avoidance of strain. There is thus an internal angular strain in triptycene amounting to some 63°, compared with about 75° in bicyclo-[2,2,1]heptane and zero in bicyclo[2,2,2]octane (see below). The other feature of special interest in the triptycenes is their possession of three benzene rings incapable of interacting with the 1-position by a resonance mechanism, but exerting whatever polar influence (presumably an electron-attracting inductive effect) may be at their disposal.[14] The summation of these effects might well make the triptycyl cation the least favored of all those studied as yet. Such a position is entirely consistent with the evidence thus far developed.

Methods hitherto tried for the formation of the triptycyl free radical have failed. Since the question is no longer one of any similarity between triptycyl and triphenylmethyl but rather whether the triptycyl radical may not be considerably more unstable than an ordinary aliphatic free radical,[2c] it has seemed of interest to attempt to prepare the triptycyl free radical by the decomposition of the appropriate diacyl peroxide. The preparation of the requisite compounds has afforded an opportunity for a more extensive exploration of the chemistry of triptycene than has occurred heretofore.

Preparation of Compounds

Methyl triptoate (II, X = $COOCH_3$) was prepared by the general sequence of reactions used previously except for a few modifications. The initial Diels–Alder addition of quinone proceeded more satisfactorily to methyl anthroate than to anthroic acid (77% yield compared to 26%). From 1-carbomethoxytriptycenequinone the dioxime was obtained in 70% yield, but was accompanied by at least four other compounds in minor amounts. These compounds were not investigated further, but one of them, a green substance, was identified as one of the monoximes in the form of the nitrosophenol. Stannous chloride proved to be the most satisfactory reagent for reducing the dioxime to the diamine, which could be obtained analytically pure only as its diacetyl derivative. The deamination of the diamine with hypophosphorous acid proceeded well, yielding as the only isolated by-product a little methyl 2-hydroxytriptoate, which probably arose from monoxime in the dioxime and aminophenol in the diamine. Triptaldehyde was also prepared from 9-anthraldehyde as starting material by the same sequence of reactions.

Except for a not unexpected degree of steric hindrance, the series of derivatives to which triptoic acid gives rise is entirely normal and includes the acid chloride, anhydride, amide, azide and diacyl peroxide. The azide, though unusually stable, could be converted into the isocyanate by long heating in the solid state, and the isocyanate was hydrolyzed to the amine, 1-aminotriptycene. The ester was also reduced to a primary alcohol by lithium aluminum hydride.

Photodimers

9-Anthraldehyde, methyl 9-anthroate and the adduct of the latter with benzoquinone all show the property of conversion by ultraviolet light into high-melting, insoluble products the first two of which on heating are reconverted into the original substances. Unsuccessful attempts were made to prepare a derivative of the anthraldehyde dimer (*e.g.*, with *p*-phenylenediamine) which would indicate whether it was a head-to-head or head-to-tail dimer. The compound showed a strong band in the infrared at 5.8 μ, shifted from the 5.95 μ peak of the monomer. This is presumably the same material as was observed but not isolated by Hinkel, Ayling and Beynon.[15] The photodimer of methyl anthroate, m.p. 218–220°, was not further investigated.

Unlike the anthracene compounds, the yellow adduct is not dimerized by irradiation in solution but only in the solid state, a fact which suggests that, as with the formation of the truxillic acids, the juxtaposition of groups in the crystal is important in determining the mode, or even the occurrence, of dimerization. The insoluble white product decomposes at 310°. It shows a shift of its carbonyl absorption to the unconjugated position at 5.8 μ. One suspects dimerization at the double bond of the oxygen-bearing ring in this case and 1,4-dimerization in the cases of the anthracenes.

The Hydroxy Esters

The presence of an hydroxyl group at position 2 in the triptycene ring has two noteworthy effects upon the properties of the triptoic esters: it greatly accelerates their alkaline hydrolysis, and it produces strong hydrogen bonding which modifies the infrared absorption of both the hydroxyl and the carbonyl groups. Whereas heating for one hour with potassium hydroxide in diethylene glycol at 130° is required to effect the hydrolysis of methyl triptoate, it required only two minutes warming with sodium hydroxide in aqueous methanol to hydrolyze methyl 2-hydroxytriptoate in good yield. Evidence in the present case permits either of two interpretations, that the reaction proceeds *via* the lactone or that the direct attack of hydroxyl ion upon the ester carbonyl group is facilitated by hydrogen bonding between the oxygen of the carbonyl group and the 2-hydroxyl group.

The infrared absorption spectrum of methyl 2-hydroxytriptoate (F, Fig. 1) shows a single broad band at 3.09 μ and none at the normal hydroxyl position of 2.8 μ. The persistence of this situation

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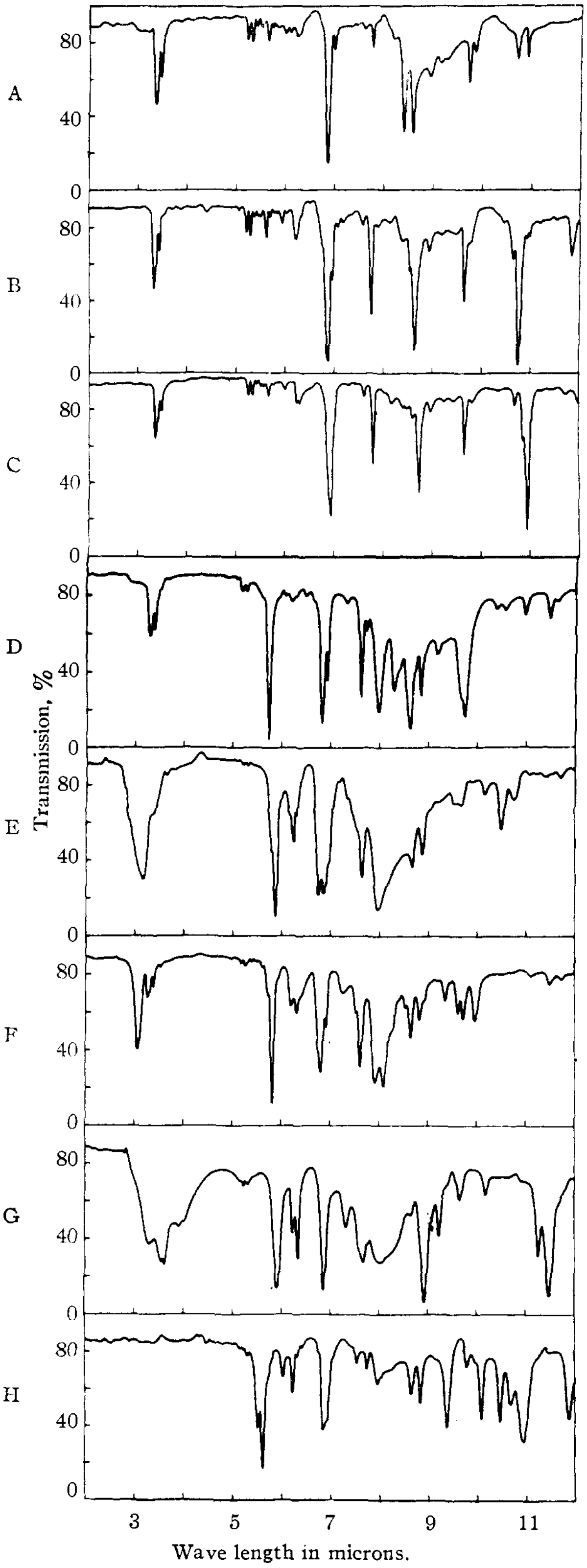
[14] B. M. Wepster. *Rec. trav. chim.*, **71**, 1159. 1171 (1952), has shown that the phenyl group in benzoquinuclidine exerts an inductive base-weakening effect of about three powers of ten upon the bridgehead nitrogen atom.

[15] L. E. Hinkel, E. E. Ayling and J. H. Beynon, *J. Chem. Soc.*, 344 (1936).



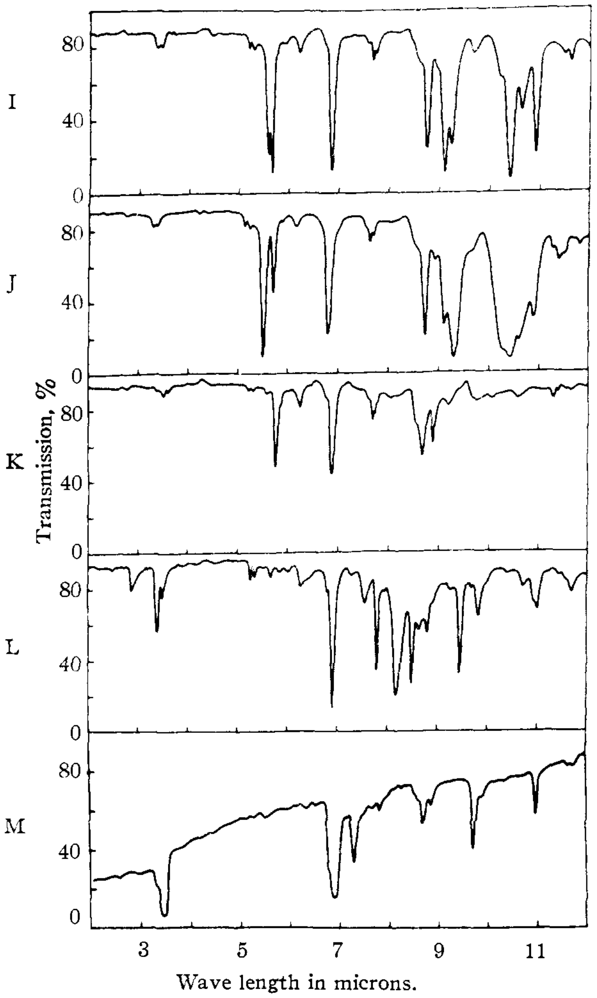


Fig. 1.—Infrared spectra of triptycene derivatives: A, II (X = H); B, II (X = Br); C, II (X = I); D, II (X = $COOCH_3$); E, 1-carbomethoxytriptycenehydroquinone; F, 1-carbomethoxy-2-hydroxytriptycene: G, 2-hydroxytriptoic acid; H, lactone of G; I, ditriptoyl peroxide; J, triptoic anhydride; K, triptycyl triptoate; L, 1-hydroxytriptycene; M, compound X (Nujol suspension). Spectra A–D, F and L were taken in carbon tetrachloride; E and G–K in chloroform.

with increasing dilution is consistent with internal hydrogen bonding. Methyl triptoate (D, Fig. 1) has a single sharp peak at 5.74 μ; methyl 2-hydroxytriptoate has a very small peak at this wave length and an intense, sharp peak at 5.80 μ. The same effect is observed in the spectra of 2-hydroxytriptoic acid (G) and of 1-carbomethoxytriptohydroquinone (E). The hydrogen bonding indicated by these shifts is similar to that observed in salicylic acid and its derivatives.[16]

The Decomposition of Ditriptoyl Peroxide

Ditriptoyl peroxide was decomposed at 80° in the absence of oxygen in benzene solution and an effort was made to account quantitatively for the products. Carbon dioxide was swept through with nitrogen and absorbed in an ascarite tube; triptoic acid, the only acidic product, was isolated by extraction of the solution with alkali, and the remaining products were separated by adsorption on alumina, recrystallization and sublimation. De-

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(16) R. S. Rasmussen and R. R. Brattain, This Journal, **71**, 1073 (1949).

spite the completeness of the original alkali extraction, more triptoic acid appeared in the course of the chromatographic separation, evidently from the decomposition or hydrolysis of some non-acidic reaction product. Table I lists the products from two of these quantitative decompositions, and has several points of considerable interest.

The closeness of the carbon dioxide yield to 50 mole per cent. and the appearance of 45 mole per cent. of triptycene, suggests the concerted decomposition into three fragments so often postulated in such studies as these. In a decomposition conducted in the presence of iodine there was no triptycene produced, but it was replaced by 41 mole per cent. of 1-iodotriptycene, an observation consistent with the occurrence of the triptycyl radical as a common precursor of both products. The triptycene appears to be formed by the capture of hydrogen from benzene, with diphenyl as an accompanying product.

The sum of the carbon dioxide accounted for in the ascarite tube, and as triptoate still leaves 16–19% unaccounted for. This corresponds roughly in amount with two unexpected products, hydroxytriptycene and the unextracted triptoic acid which is obtained from the column. Since triptycyl triptoate was found by experiment to be far too resistant to hydrolysis to be the precursor of the second batch of triptoic acid, it is attractive to postulate a decomposition product of the peroxide which on hydrolysis readily yields one mole of triptoic acid, one mole of hydroxytriptycene and one mole of carbon dioxide. Such a product would escape the first extraction and in hydrolyzing on the column would produce the observed acid and alcohol and would evolve a like amount of carbon dioxide which would be lost. From the decomposition of *p*-methoxy-*p'*-nitrobenzoyl peroxide in a polar solvent Leffler[17] isolated a product with one carboxyl group inverted which readily hydrolyzed to yield *p*-methoxyphenol, carbon dioxide and *p*-nitrobenzoic acid. The corresponding reaction in our case would be

$$\text{TrCOO}-\text{OOCTr} \longrightarrow \text{TrCOO}-\text{COOTr} \xrightarrow{\text{H}_2\text{O}}$$
$$\text{TrCOOH} + \text{CO}_2 + \text{TrOH}$$
$$[\text{Tr} = \text{triptycyl}]$$

The predisposing factors to this reaction—unsymmetrical substitution of the peroxide and a polar reaction medium—as recognized by Leffler are notably lacking in the present case. We can only suggest that some small amount of polar decomposition in diacyl peroxides may be of more common occurrence than has been supposed, since its products are easily confused with those derivable from radical decomposition.[18]

Compound X, referred to in Table I, is an insoluble powder obtained by filtration of the original solution after decomposition of the peroxide. It melted with decomposition at 520–525° in a sealed tube, showed an infrared absorption spectrum resembling that of other 1-substituted triptycenes, and was obtained in amounts too small for further study. It might well be 1,1-ditriptycyl.

TABLE I

PRODUCTS OF DECOMPOSITION OF DITRIPTOYL PEROXIDE IN BENZENE AT 80.07°

Compound	Run 1 (18 hr.) Millimole	Run 1 (18 hr.) Mole %[a]	Run 2 (33 hr.) Millimole	Run 2 (33 hr.) Mole %[a]
Original peroxide	0.703	100	0.928	100
CO_2	.664	47.2	.975	52.5
Diphenyl	Present		Present	
Triptycene	.637	45.2	.842	45.3
1-Triptycyl triptoate	.040	5.7[c]	.057	6.1[d]
1-Hydroxytriptycene	.240	17.1	.323	17.4
Triptoic acid (from extraction)	.211	15.0	.200	10.8
Triptoic acid (from column)	.220	15.6	.325	17.5
Compound X	.007	1.0[b]	.020	2.2[b]
CO_2 accounted for		80.7		83.8
CO_2 not accounted for		19.3		16.2

[a] Calculated as % of the total CO_2 or triptycyl groups accounted for. [b] Calculated on the assumption that X is ditriptycyl. [c] 2.85% of total CO_2. [d] 3.05% of total CO_2.

The decomposition of the peroxide in the presence of iodine was not carried out quantitatively except for the isolation of the iodotriptycene (41%). The isolation of the latter involved separation from 17.6 mole % of 1-hydroxytriptycene, which is so close to the amount obtained in the absence of iodine as to support the idea that it results from a polar decomposition which is unaffected by the presence of iodine.

The decomposition of ditriptoyl peroxide was of the first order to well over 90% of total reaction, the rate constant at 80° being 1.42×10^{-4} sec.$^{-1}$. Table II shows a comparison of this peroxide with three others whose rates have been measured at the same temperature. The rate constant for diapocamphoyl peroxide is from the work of Sager.[19] If we assume that acetyl, triptoyl and apocamphoyl peroxides all decompose by the concerted mechanism, then the ease or difficulty of formation of the related alkyl free radicals should be reflected in the rates of decomposition. In this case there is no great difference between the tertiary bridgehead radicals and the methyl radical in ease of formation. However, judging by the much greater speed of

TABLE II

FIRST-ORDER RATE CONSTANTS FOR DECOMPOSITION OF DIACYL PEROXIDE

Peroxide	$k_1 \times 10^5$, sec.$^{-1}$	Temp., °C.	Solvent
Apocamphoyl	23[a]	80	Benzene
Triptoyl	14.2	80	Benzene
Acetyl	7.3[b]	80	Toluene
Benzoyl	3.3[c]	79.8	Benzene

[a] W. F. Sager, Thesis, Harvard University, 1948. [b] O. J. Walker and G. L. E. Wild, *J. Chem. Soc.*, 1132 (1937). [c] K. Nozaki and P. D. Bartlett, THIS JOURNAL, **68**, 1686 (1946).

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[17] J. E. Leffler, THIS JOURNAL, **72**, 67 (1950).

[18] It will be noted also that if only 66% of the peroxide decomposes by a free radical mechanism, some of the triptoate radicals postulated in the three-body mechanism must lose carbon dioxide subsequent to their formation in order to account for the amount of triptycene and carbon dioxide produced.

[19] W. F. Sager, Thesis, Harvard University, 1948.

decomposition of the peroxides of trisubstituted acetic acids, we must conclude that the bicyclic structure largely eliminates from tertiary radicals that considerable degree of stabilization by which they normally excel the methyl radical.

1-Iodotriptycene in Ionic Reactions

1-Iodotriptycene was recovered after heating under reflux for 48 hours with silver nitrate in 81.8% aqueous ethyl alcohol by volume, and no opalescence or precipitate was noted at any time. This experiment, previously carried out with 1-bromotriptycene with the same result, was repeated because of the generally greater reactivity of iodo compounds. For a rough comparison with quantitative rate determinations on other compounds, we may attempt to set a maximal value on the ionization rate constant of iodotriptycene. If it be assumed that opalescence would be detectable when the solubility product of silver iodide (3.2×10^{-17}) was exceeded by a factor of ten, we can conclude that the iodide ion concentration did not reach 2×10^{-14} *M* in our experiment. This means that the first-order rate constant for ionization of 1-iodotriptycene is less than 3×10^{-17} sec.$^{-1}$ at 78°. Using the figures given by Doering and co-workers,[5b] and assuming a near equivalence of rates in 70% aqueous dioxane and 80 and 81.6% aqueous ethanol, we conclude that the rate constants for the ionization of *t*-butyl bromide, 1-bromobicyclo-[2,2,2]octane, and 1-iodotriptycene (maximal rate) stand in the ratio of about $1:10^{-6}:10^{-15}$. To the extent that the replacement of bromine by iodine tends to increase the reactivity and to the extent to which silver ion accelerates reaction by direct attack on the halogen atom, the properly comparable figures would show an even greater gap between the bicyclo[2,2,2]octyl and triptycyl compounds.

From the results of Wepster[14] on the inductive effect of a benzene ring on the basic strength of quinuclidine we might anticipate that the three phenyl groups of the triptycyl cation would destabilize it by at least nine powers of ten in an equilibrium or rate constant in comparison with the bicyclo[2,2,2]octyl cation. The stiffening effect of the phenyl groups upon the internal bond angles, referred to in the introduction, would produce an effect over and above this inductive effect. We expect, therefore, that it will require conditions of more than slightly increased vigor to detect solvolytic reactivity in the 1-halotriptycenes.

Experimental

The microanalyses were performed under the direction of S. M. Nagy at the Massachusetts Institute of Technology. All melting points below 300° were taken in a melting point bath and are corrected. Those above 300° were taken on a block and are not corrected.

9-Anthraldehyde was prepared by the method of Fieser, Hartwell and Jones.[20] It melted at 105–105.5°.

Dimer of 9-Anthraldehyde.—A solution of 2 g. of 9-anthraldehyde in 30 ml. of chloroform in a quartz flask was exposed to a sun lamp for 18 hours. A precipitate of 1.12 g. which formed on the walls was collected by filtration and washed with more chloroform. Recrystallization from 75 ml. of benzene yielded 0.72 g. of large cubic crystals, melting at 185–186°. The melt on cooling resolidified to 9-anthraldehyde melting at 105–105.5°.

Anal. Calcd. for $C_{30}H_{20}O_2$: C, 87.35; H, 4.89. Found: C, 87.61; H, 5.02.

Attempts to form the 2,4-dinitrophenylhydrazone yielded only the 2,4-dinitrophenylhydrazone of 9-anthraldehyde, melting point 260–261°.

Anal. Calcd. for $C_{21}H_{14}ON_4$: C, 65.28; H, 3.65. Found: C, 65.69; H, 3.80.

9-Anthroic acid was prepared by the method of Latham, May and Mosettig[21a] using anthracene purified by codistillation with ethylene glycol[21b] and reagent grade oxalyl chloride. One recrystallization from ethanol gave yellow needles melting at 218–219° with decarboxylation in a yield of 55%.

Because of the ready availability of 9-anthraldehyde, numerous attempts were made to oxidize this to the acid. The most successful procedure, using silver oxide and ferric chloride, was still less reliable than the synthesis with oxalyl chloride.

Keto Form of 1-Carboxytriptycenehydroquinone.—The solution of 1.3 g. of 9-anthroic acid and 2.6 g. of reagent grade benzoquinone in 30 ml. of dioxane was heated under reflux for 24 hours, cooled and poured into water. The precipitate thus formed was extracted with ether, the ether removed and the residue was washed with 400 ml. of boiling water to remove quinone. Recrystallization of the brown residue from ethanol gave 0.5 g. of small light yellow prisms which melted to a red oil at 196–197°, a yield of 26%.

1-Carboxytriptycenequinone.—The above adduct, 0.4 g., was dissolved in 12 ml. of acetic acid, heated and 2 ml. of concentrated hydrochloric acid was added, resulting in a lightening of color. The solution was cooled, 12 ml. of water being added. To this solution was now added dropwise and with stirring a solution of 0.1 g. of sodium bromate in 4 ml. of water. An orange precipitate settled out, weighing 0.38 g. and melting at 258–260°. Recrystallization from 4 ml. of ethanol gave 0.32 g. of shiny, orange-brown crystals melting at 274–276°, a 79% yield from the adduct.

Anal. Calcd. for $C_{21}H_{12}O_4$: C, 76.82; H, 3.69. Found: C, 76.54; H, 3.91.

Methyl 9-anthroate was prepared from 9-anthroic acid by diazomethane. Two recrystallizations from methanol (10 ml. of solvent per gram of ester) yielded large prisms melting at 112.7–113.2°. Exposure to sunlight converts this material into a compound which melts at 218–219°, and possesses a sharp band in the infrared at 5.75 μ.

A 28% yield of this ester, melting at 111–112°, was also obtained by the method of Newman by pouring a solution of 9-anthroic acid in 100% sulfuric acid into excess of absolute methanol cooled in an ice-bath.[22]

Keto Form of 1-Carbomethoxytriptycenehydroquinone.—A solution of 77 g. of methyl 9-anthroate and 100 g. of reagent grade benzoquinone in 385 ml. of dry benzene was heated under reflux for 40 hours. (It is essential that the ester be highly pure.) The benzene was removed by steam distillation and the residue was washed by decantation with boiling water to remove the excess benzoquinone. The crude yellow product was dissolved in 600 ml. of chloroform, treated with Norit and filtered. To the hot chloroform solution was added 400 ml. of ligroin (b.p. 60–90°). Upon cooling, 71 g. of large yellow prisms, melting at 199.4–200.8° to a red oil, was obtained. A second crop of 16 g. was obtained from the mother liquor, representing a yield of 77.5%.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.75; H, 4.83.

Effect of Radiation upon Keto Form of 1-Carbomethoxytriptycenehydroquinone.—Upon exposure to sunlight or to ultraviolet light, the crystals of the adduct fall to a fine white powder, $(C_{22}H_{16}O_4)_x$. A 40-mg. sample of the adduct in a vial under an atmosphere of purified nitrogen was converted to the white form in 15 minutes. Irradiation of a solution of the adduct in chloroform for two hours failed to effect conversion to the white form. The compound decomposes at 310° and its infrared absorption spectrum shows bands at 5.75 and 5.8 μ. Its insolubility in all common

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(20) L. F. Fieser, J. L. Hartwell and J. E. Jones. *Org. Syntheses*, **20**, 11 (1940).

(21) (a) G. Latham, Jr., E. L. May and E. Mosettig, This Journal, **70**, 1079 (1948); (b) L. F. Fieser, "Experiments in Organic Chemistry," D. C. Heath and Co., New York, N. Y., 1941, p. 345.

(22) M. S. Newman, This Journal, **63**, 2431 (1941).

organic solvents prevented the determination of the molecular weight.

Anal. Calcd. for $(C_{22}H_{16}O_4)_x$: C, 76.73; H, 4.68. Found: C, 76.79; H, 4.98.

1-Carbomethoxytriptycenehydroquinone.—To a solution of 71 g. of the keto form of 1-carbomethoxytriptycenehydroquinone in 355 ml. of glacial acetic acid, heated on the steam-bath, was added 15 ml. of concentrated hydrochloric acid with stirring. The color of the solution lightened at once, and after ten minutes the hydroquinone started to precipitate. Stirring was continued for one hour. After cooling for 12 hours, the product was collected and dried in a vacuum, giving 51 g. of white needles melting at 265–266°. An additional 19 g. of material was obtained from the mother liquor by dilution with water. Recrystallization of this fraction from acetic acid gave another 16.5 g. of pure material, a total of 67.5 g. representing a yield of 94.5%.

Anal. Calcd. for $C_{22}H_{16}O_4$: C, 76.73; H, 4.68. Found: C, 76.70; H, 4.87.

1-Carbomethoxytriptycenequinone.—A solution of 19.3 g. of sodium bromate in 240 ml. of water was added dropwise and with stirring to a solution of 102 g. of the hydroquinone in 1020 ml. of acetic acid at room temperature, two hours being required for the addition. After one hour the product started to precipitate. After all the sodium bromate solution had been added, an additional 100-ml. portion of water was added dropwise. The flask was then cooled overnight. The orange product was collected by filtration and washed with 75 ml. of cold acetic acid. Recrystallization from 530 ml. of acetic acid gave 72 g. of large orange prisms melting at 225–226°. A small amount of additional quinone could be obtained from the mother liquor of the reaction mixture, but required four recrystallizations from acetic acid to effect purification. The 72 g. of quinone represent a yield of 71%.

Anal. Calcd. for $C_{22}H_{14}O_4$: C, 77.18; H, 4.12. Found: C, 77.42; H, 4.24.

An attempted hydrolysis of 1-carbomethoxytriptycenequinone by potassium hydroxide in methanol–water yielded only 9-anthroic acid as an isolated product.

Dioxime of 1-Carbomethoxytriptycenequinone.—A solution of 50 g. of 1-carbomethoxytriptycenequinone and 100 g. of hydroxylamine hydrochloride (recrystallized from water) in 3.2 l. of methanol was heated under reflux for 24 hours. The dark methanol solution was filtered from a small amount of orange solid and poured into 12 liters of water. After 12 hours the tan precipitate was collected by filtration and dried, amounting to 53 g. The dioxime, a light yellow powder, was obtained in a yield of 38 g. (70%) after three washings with benzene. Recrystallization from benzene and methanol gave large yellow prisms decomposing from 260° to 360° depending upon the rate of heating.

Anal. Calcd. for $C_{22}H_{16}O_4N_2$: C, 70.96; H, 4.33; N, 7.52. Found: C, 71.96; H, 4.86; N, 7.53.

By-products of the Oxime Formation.—The benzene solution from the washing of the dioxime was subjected to a chromatographic separation on alumina (Merck) giving a multicolored column. The bands were eluted by benzene, fractions being cut by color. The first fraction upon recrystallization from benzene and petroleum ether (b.p. 40–60°) yielded a green compound and a white one. These were separated mechanically and purified by further recrystallizations from the same solvent pair. The green compound decomposed at 240° and corresponded in analysis to the nitrosophenol.

Anal. Calcd. for $C_{22}H_{15}O_4N$: C, 73.94; H, 4.23; N, 3.92. Found: C, 73.66; H, 4.67; N, 3.89.

The white compound contained halogen, probably the result of the addition of hydrogen chloride to the quinoid system, and melted at 275–278°. The second fraction from the column gave an orange solid; recrystallization from tetrahydrofuran and ligroin produced orange needles melting at 280–282°. The third through ninth fractions consisted of semi-solid material and oils. The tenth was a green solid, decomposing at 250°. These by-products were not further investigated.

1-Carbomethoxy-2,5-diaminotriptycene Dihydrochloride.—The dioxime, 38 g., obtained by the benzene extraction described above was treated with 1330 ml. of hot methanol and filtered from a small amount of white solids. To the refluxing yellow-orange methanolic filtrate was added a solution of 167 g. of stannous chloride dihydrate in 380 ml. of concentrated hydrochloric acid. The solution was stirred at reflux temperature for 20 minutes during which time the dihydrochloride started to precipitate. After cooling the mixture for six hours, the product was collected by filtration and dried in a vacuum. This procedure yielded 21 g. of a product corresponding to a yield of 49.5%. The dihydrochloride sintered at 265° and melted at 285–289° with bubbling. It was quite insoluble in hot water.

1-Carbomethoxy-2,5-diaminotriptycene.—A mixture of 0.5 g. of the dihydrochloride, 1.0 g. of anhydrous sodium carbonate and 10 ml. of absolute methanol was refluxed for one hour. The mixture was cooled, 1.5 g. of calcium oxide was added, and the alcohol was distilled off. To the residue was added 10 ml. of benzene; the mixture was filtered hot and the benzene removed under reduced pressure. By carrying out the above operation under nitrogen, 247 mg. of a white solid was obtained, melting with bubbling at 188–190°. Further purification of this compound proved very difficult.

Anal. Calcd. for $C_{22}H_{18}O_2N_2$: C, 77.17; H, 5.30. Found: C, 78.92; H, 5.74.

1-Carbomethoxy-2,5-diacetamidotriptycene.—A solution of 100 mg. of the diamine and eight drops of acetic anhydride in 6 ml. of benzene was heated under reflux for 2 hours. The white crystalline precipitate that formed during this time was collected by filtration and recrystallized from methanol, melting point 246.5–247.5°.

Anal. Calcd. for $C_{26}H_{22}O_4N_2$: C, 73.22; H, 5.20. Found: C, 72.65; H, 5.30.

1-Carbomethoxytriptycene.—A solution of 34.5 g. of 1-carbomethoxy-2,5-diaminotriptycene dihydrochloride in one liter of 50% hypophosphorous acid was added dropwise and with stirring to a solution of two liters of 50% hypophosphorous acid containing 35 g. of sodium nitrite, kept below −15° by a Dry Ice–acetone-bath. The solution turned red after three minutes, and after ten minutes nitrogen started to evolve with a characteristic frothing. The addition required three hours, and the mixture was stirred an additional three hours at −15°. After the addition of three kilograms of ice, the mixture was stirred one more hour. The flask was then kept at 0° overnight. The mixture was extracted with benzene and the benzene layer was washed with 10% sodium hydroxide, 10% hydrochloric acid and water. Evaporation of the benzene solution to dryness yielded 24.1 g. of crude product. This material was dissolved in 500 ml. of carbon tetrachloride and adsorbed on a column of 150 g. of alumina (Merck). The desired ester was easily eluted, the first fraction of 600 ml. of eluate containing all the ester, 19.5 g. of white crystalline material melting at 204–205°, a yield of 75%.

Anal. Calcd. for $C_{22}H_{16}O_2$: C, 84.59; H, 5.16. Found: C, 84.95; H, 5.34.

The second and third fractions consisted of small amounts of oil. The fourth and fifth fractions contained 3.3 g. of brown solid. Repeated recrystallizations from methanol yielded small white needles melting at 244.0–244.2°. This compound shows strong absorption in the infrared at 3.09 μ and at 5.80 μ and yields analyses corresponding to **1-carbomethoxy-2-hydroxytriptycene**. See Fig. 1, spectrum D.

Anal. Calcd. for $C_{22}H_{16}O_3$: C, 80.48; H, 4.91. Found: C, 80.87, 80.96; H, 5.09, 5.03; N, 0.

1-Carboxy-2-hydroxytriptycene.—Seven drops of 10% sodium hydroxide were added to a solution of 60 mg. of 1-carbomethoxy-2-hydroxytriptycene in 2 ml. of methanol. Addition of 2 ml. of water was followed by two minutes of heating on the steam-bath. The clear solution was cooled and acidified, giving a precipitate. Upon reheating, the material dissolved. Slow cooling now yielded 50 mg. of small white needles, melting at 254–256° with bubbling. Two recrystallizations from methanol-water gave white rosettes melting at 258–261° with bubbling.

Anal. Calcd. for $C_{21}H_{14}O_3 \cdot {}^1/_2H_2O$: C, 78.00; H, 4.68. Found: C, 78.19, 78.37; H, 5.00, 4.57.

Lactone of 1-Carboxy-2-hydroxytriptycene.—A sample of 130 mg. of the hydroxy acid was heated at 260° and atmospheric pressure for ten minutes in a sublimation tube. The fine feathery sublimate that formed on the tube was washed down with chloroform and the solvent was removed in a current of air. The residue was sublimed at a pressure of 0.4 mm. and 190°, giving a mixture of the lactone and hydroxy acid. The mixture was separated by chromatography on a 1.6 g. column of alumina, giving 54 mg. of the lactone. Two recrystallizations from benzene–ligroin gave short, thick needles melting at 270–271°.

Anal. Calcd. for $C_{21}H_{12}O_2$: C, 85.12; H, 4.08. Found: C, 85.09; H, 4.30.

No bubbling was observed on heating a sample of the hydroxy ester at 300° for 15 minutes, but the infrared absorption spectrum of the residue was that of a mixture of the starting material and the lactone.

1-Carboxytriptycene (Triptoic Acid).—To a solution of 7.4 g. of potassium hydroxide in 100 ml. of diethylene glycol was added 3.0 g. of 1-carbomethoxytriptycene, and the solution was heated at 130° for one hour. The solution was poured into 400 ml. of water, treated with Norit, filtered and acidified, giving 2.8 g. of 1-carboxytriptycene (triptoic acid). Large colorless prisms were obtained by recrystallization from dioxane–ligroin, melting at 355–356.5°, a yield of 91%.

Anal. Calcd. for $C_{21}H_{14}O_2$: C, 84.54; H, 4.73. Found: C, 84.69; H, 4.98.

Attempted Decarboxylation of Triptoic Acid. (a) By Quinoline and Copper Chromite.—To a solution of 200 mg. of triptoic acid in 5 ml. of quinoline was added 50 mg. of copper chromite, and the mixture was heated at 250° for four hours. After cooling, the mixture was poured into dilute sulfuric acid and filtered. The collected precipitate was treated with hot 10% sodium hydroxide and filtered. Acidification of the filtrate yielded triptoic acid, 152 mg. after recrystallization from dioxane-ligroin, melting at 355–356°.

(b) By Soda Lime Pyrolysis.—A finely powdered mixture of 200 mg. of sodium triptoate and 500 mg. of soda lime was heated in a sublimation tube at a pressure of one mm. Over a period of eight hours the temperature of the bath was raised to 350°. The expected product, triptycene, would have sublimed, if formed. No sublimate was visible. The tube was cooled, the residue treated with water, filtered, and acidified, resulting in the quantitative recovery of triptoic acid.

Triptoic anhydride was obtained in a preliminary attempt to prepare triptoyl chloride. The acid was heated under reflux with thionyl chloride, the cooled solution was poured on ice, and the precipitate collected. Repeated recrystallization from benzene–ligroin effected the purification of the anhydride which melted at 354–355°.

Anal. Calcd. for $C_{42}H_{26}O_3$: C, 87.17; H, 4.53. Found: C, 87.45; H, 4.78.

Triptoyl Chloride.—A solution of 5.45 g. of triptoic acid in 35 ml. of dry dioxane was added dropwise over two hours to a refluxing solution of 40 ml. of purified thionyl chloride. The solution was refluxed an additional six hours, the solvents were removed under reduced pressure, and the residue was recrystallized from carbon tetrachloride–ligroin, giving a first crop of 4.58 g. of large flat needles melting at 190–192°, and a second crop of 0.8 g., a yield of 93%. Two recrystallizations from carbon tetrachloride–ligroin gave a product melting at 193–194°. This compound is only slowly hydrolyzed upon exposure to the air. The pure material was obtained in 86% yield from the acid.

Anal. Calcd. for $C_{21}H_{13}OCl$: C, 79.62; H, 4.14. Found: C, 79.22; H, 4.25.

Triptamide.—The addition of one drop of concentrated ammonia solution to 20 mg. of triptoyl chloride in 1 ml. of ether yielded a white precipitate. Evaporation of the solvents and recrystallization of the residue from 20 ml. of ethanol gave the amide as colorless prisms melting at 298–300°.

Triptazide.—A solution of 78 mg. of sodium azide in 0.3 ml. of water was added dropwise and with stirring to a solution of 316 mg. of triptoyl chloride in 4 ml. of acetone, cooled to 0°. After 30 minutes the mixture was poured into 25 ml. of water and filtered. The white solid, dried over phosphorus pentoxide, weighed 316 mg., a yield of 98%. With slow heating it turned to a clear melt at 245–247°. A sample recrystallized from carbon tetrachloride–ligroin, small white prisms, melted at 247–248°. The infrared spectrum of this material shows the characteristic bands at 4.7 and 5.81 μ, and the total absence of any acid chloride band at 5.6 μ.

Triptycyl Isocyanate.—The azide is only slowly converted to the isocyanate in refluxing xylene. Conversion to the isocyanate was best performed as follows: the azide was placed in a vial and heated in a drying pistol for 24 hours at 100°, giving triptycyl isocyanate, melting at 248–249°, in quantitative yield. The infrared spectrum shows the characteristic band at 4.45 μ and the total absence of the azide bands at 4.7 and 5.81 μ.

Triptycylamine.—To a solution of 8 g. of potassium hydroxide in 50 ml. of 95% ethanol was added 0.62 g. of the isocyanate and the solution was refluxed for 21 hours. The solution was poured into water, giving a silver-white precipitate. The product was extracted with ether, the ethereal solution was washed with water, and then dried over magnesium sulfate. Removal of the ether gave 0.525 g. of the amine, melting at 218–220°, a yield of 93%. Recrystallization from ligroin gave large colorless prisms melting at 221–221.5°, an over-all yield of 81% of pure material.

Anal. Calcd. for $C_{20}H_{15}N$: C, 89.18; H, 5.61; N, 5.20. Found: C, 88.98; H, 5.82; N, 5.08.

The hydrochloride darkens at 320° and decomposes above 340°.

In the hope of obtaining an azo compound which might yield the triptycyl free radical on decomposition, an unsuccessful attempt was made to condense triptycylamine with nitrosobenzene.

1-Hydroxymethyltriptycene.—A solution of 312 mg. of 1-carbomethoxytriptycene in 15 ml. of ether was added to a slurry of 300 mg. of lithium aluminum hydride in 10 ml. of ether. The flask was left at room temperature with occasional swirling for 24 hours. Moist ether was added to decompose the excess reductant, followed by 5% sulfuric acid. The ether layer was separated, washed twice with water and dried over magnesium sulfate. Removal of the ether gave 280 mg. of the alcohol, melting at 235–239°, representing a yield of 98%. Recrystallization from benzene gave 248 mg. of crystals melting at 242–243°, a yield of 87.5%.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.70; H, 5.67. Found: C, 88.65; H, 5.84.

Triptycene.—Triptycene was prepared from 2,5-diaminotriptycene dihydrochloride in over 75% yield by the method used to prepare 1-carbomethoxytriptycene. Recrystallization from carbon tetrachloride–ligroin gave long rectangular prisms melting at 254.5–255°.

1-Formyltriptycene (triptaldehyde) was prepared by a sequence of reactions similar to that used for 1-triptoic acid. From two grams of 1-formyltriptycenequinone, a compound previously prepared by Bartlett, Cohen, Cotman, Kornblum, Landry and Lewis,[2b] there was isolated 92 mg. of 1-formyltriptycene from the final chromatographic separation on alumina. Recrystallization from methanol gave small prisms melting at 248–252°. The infrared absorption spectrum showed the triptycene bands and a strong band at 5.80 μ. Evidently neither the oxime formation from the quinone nor the reduction of the dioxime affected the aldehyde group.

Ditriptoyl Peroxide.—To a solution of 2.30 g. (7.26 millimoles) of triptoyl chloride in 110 ml. of anhydrous ether, cooled to 0° and stirred with a glass propeller-type stirrer. was added eleven drops (0.55 ml.) of water, followed by 0.460 g. (5.43 millimoles) of 93.5% sodium peroxide. The mixture was stirred for 36 hours at 0°. The ethereal solution and precipitate were decanted from a small amount of unreacted sodium peroxide and the ether was removed in a current of dry air. The residue was taken up in 100 ml. of benzene to which was added a few drops of water and the material adsorbed on a 25-g. column of alumina. The impurities, acid chloride and anhydride, are the most strongly retained on the column. Elution with 75 ml. of benzene removed all the peroxide from the column. Removal of the benzene under reduced pressure gave 1.62 g. of ditriptoyl peroxide of 95.5% purity, as determined by iodometric titration in acetone. This corresponds to a yield of 71%.

Anal. 0.0338 g. of peroxide required 10.75 ml. of 0.0101 *N* thiosulfate solution; purity, 95.5%.

Recrystallization from benzene yielded large colorless prisms of 99.4% purity after two days drying at 1 mm. pressure, over calcium chloride. With slow heating the compound softened at 294–296° with the evolution of carbon dioxide.

Anal. 0.0263 g. of peroxide required 8.72 ml. of 0.0101 *N* thiosulfate solution; purity, 99.4%.

Analysis of Ditriptoyl Peroxide.—Ditriptoyl peroxide was analyzed by the method used by Sager for the peroxides of ketopinic acid and apocamphane-1-carboxylic acid.[19] Samples of approximately 30 mg. were weighed into a 50-ml. glass-stoppered erlenmeyer flask and 0.5 g. of sodium iodide was added. A small amount of Dry Ice was introduced into the loosely stoppered flask; and when most of the Dry Ice had disappeared, the stopper was lifted sufficiently to introduce 5 ml. of reagent grade acetone. The characteristic iodine color was immediately apparent, but ten minutes (in the dark) with occasional swirling was necessary for the complete solution and reaction of the peroxide. Twenty ml. of water was added, giving a clear solution which was titrated with 0.01 *N* thiosulfate solution to a starch end-point. Analysis in isopropyl alcohol solution by the method of Kokatnur and Jelling[23] was used as a check of the accuracy of the acetone method, giving results usually 0.5% higher than the purity determined by the acetone method.

Rate of the Decomposition of Ditriptoyl Peroxide.—A sample of the peroxide weighing 0.609 g. and showing a purity of 99.4% by iodometric titration was dissolved in approximately 175 ml. of benzene and 15-ml. portions were pipetted into tubes which were provided with stopcocks. The tubes were degassed by three cycles of freezing, evacuating, thawing and shaking. The tubes were heated for different time intervals in an oil thermostat at 80.00 ± 0.01°. Analysis for peroxide was carried out by quantitative transfer of the tube contents to a 50-ml. glass-stoppered erlenmeyer flask, evaporation of the solvent in a current of dry air, and titration of the sample with 0.01 *N* thiosulfate solution by the method described above. The reaction was cleanly of the first order, the ten experimental points covering up to 96.5% of the total reaction showing no deviation from a straight line when the logarithm of the peroxide concentration was plotted against time. The first-order rate constant for the decomposition at 80° is 1.42×10^{-4} seconds^{-1}.

Analysis of the Products of the Decomposition of Ditriptoyl Peroxide.—For the purpose of determining the products of decomposition, a solution of ditriptoyl peroxide was prepared in freshly distilled benzene in an evacuated sealed flask having an inlet and outlet tube provided with break-off joints. The solution was degassed by the standard procedure with freezing at Dry Ice temperature. It was then warmed to room temperature, shaken to redissolve all the peroxide, and immersed in an oil thermostat set at 80.07 ± 0.01°. The flask was removed after sufficient time had elapsed for the complete decomposition of the peroxide. The kinetic run showed that the peroxide was 96.5% decomposed after 6.5 hours. At the end of 18 hours the reaction should be 99.95% complete at least. One decomposition experiment was carried for 18 hours and another for 33 hours.

The evolved carbon dioxide was measured by sweeping the flask with nitrogen and collecting the gas in an absorption tube. The apparatus consisted of a bubbler, a soda lime–calcium chloride tube, the sample decomposition flask, a U-tube cooled with Dry Ice–acetone, a U-tube filled with magnesium perchlorate, the absorption tube filled with $^2/_3$ ascarite and $^1/_2$ magnesium perchlorate, another soda lime and calcium chloride tube and a Mariotte flask. The nitrogen was passed through the system at the rate of 10 ml. per minute. After 1200 ml. of nitrogen had been passed through the train, the absorption tube was weighed. This process was repeated until the tube came to constant weight.

The flask was then removed from the train and a small quantity of white, amorphous material (compound X) was isolated by filtering the solution. The filtrate was extracted with 5% sodium hydroxide solution, which upon acidification yielded triptoic acid. The benzene solution was washed with water and evaporated to dryness. The residue was dissolved in a mixture of one part of benzene to four parts of petroleum ether (b.p. 30–60°) and subjected to chromatographic separation on a column of Merck alumina prepared in petroleum ether. The first fraction to be eluted consisted of triptycene and biphenyl, which were separated by fractional sublimation. Two fluorescent bands on the column were then eluted by increasing the amount of benzene in the eluant. The first of these was identified as the ester, **triptycyl triptoate**. This compound crystallized from dioxane–ligroin in large flat plates, melting at 396–400° (sealed tube, uncorrected) and resolidifying again upon cooling. Although the analysis for carbon is not satisfactory, the infrared absorption spectrum provides strong support for the structure assigned.

Anal. Calcd. for $C_{41}H_{26}O_2$: C, 89.43; H, 4.76. Found: C, 88.49; H, 5.50.

The ester was not hydrolyzed by potassium hydroxide in diethylene glycol on heating at 130° for 15 minutes. The second fluorescent compound eluted from the column was the alcohol, **1-hydroxytriptycene**. Recrystallization yielded small colorless prisms melting at 242–243°.

Anal. Calcd. for $C_{20}H_{15}O$: C, 88.86; H, 5.22. Found: C, 88.75; H, 5.38.

A solution of 1-hydroxytriptycene in glacial acetic acid remained colorless upon the addition of concentrated sulfuric acid. The alcohol is quite insoluble in pure sulfuric acid. It dissolves upon heating to give a faintly colored solution from which the alcohol is recovered upon cooling it and dilution with water.

Further elution of the column with benzene, benzene–chloroform and chloroform yielded negligible traces of material. The alumina was then extruded and extracted with methanol containing a few drops of concentrated hydrochloric acid. Filtration, followed by evaporation of the solvent, led to the isolation of triptoic acid.

Compound X.—Compound X sublimes at 480° and decomposes at 520–525° (sealed tube). Its infrared spectrum in Nujol suspension has a band 10.95μ, in common with all the bridgehead substituted triptycene compounds. The material burns leaving no ash. Its insolubility in all solvents including camphor precluded a determination of its molecular weight. See M, Fig. 1.

The analytical data for the two quantitative product determinations are summarized in Table I.

Decomposition of Ditriptoyl Peroxide in the Presence of Iodine.—A solution of 0.768 g. (1.29 millimoles) of the peroxide and 1.65 g. (6.5 millimoles) of iodine in 60 ml. of benzene was degassed as described above, sealed, and held at 80.07° for 16 hours. The benzene solution was then washed with bisulfite solution to remove unreacted iodine. The solution was extracted with 5% sodium hydroxide solution, which yielded upon acidification 5 mg. of triptoic acid (0.0168 millimole). The benzene solution was evaporated to dryness in a current of air and the residue was subjected to fractional sublimation. The first fraction, up to 140°, was a very small amount of 1-iodotriptycene and its infrared spectrum showed the absence of diphenyl or triptycene. Fractions up to 205° consisted of a mixture of **1-iodotriptycene** and 1-hydroxytriptycene with the iodo compound predominating. Upon fractional crystallization from benzene the iodide was obtained alone in the first two crops melting at 262–265°. The compound crystallizes in beautiful, colorless prisms.

Anal. Calcd. for $C_{20}H_{13}I$: C, 63.18; H, 3.45. Found: C, 63.39; H, 3.56.

The iodide and the alcohol in the filtrate were separated by chromatography on alumina. The total weight of the iodide was 400 mg. (1.05 millimoles) a yield of 41%.

The fraction from 205–230° yielded 1-hydroxytriptycene which was purified by chromatography on alumina. The combined fractions of this alcohol totaled 123 mg. (0.455 millimole). The residue was a mixture of triptoic acid and unidentified material.

On sublimation of a mixture of 1-hydroxytriptycene and 1-iodotriptycene, the alcohol sublimed first. This fact taken in conjunction with the fact that in the original separation the iodide was obtained first indicates that the alcohol was in the original sublimate as a decomposition product of some other relatively involatile compound (see Discussion).

Behavior of 1-Iodotriptycene. (a) Toward Silver Nitrate.—A solution of 15 mg. of 1-iodotriptycene and 30 mg. of silver nitrate in 2 ml. of water and 9 ml. of absolute alcohol was refluxed for 48 hours. At the end of this time the solution was still clear and no opalescence was observed on cooling. The solution was diluted with water, extracted with benzene, and the benzene removed in a current of air. The infrared absorption spectrum of the residue was identical with that of the iodide.

(b) **Toward Silver Powder.**—A mixture of 93 mg. of the iodide and 290 mg. of silver powder was refluxed for 48 hours

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[23] V. R. Kokatnur and M. Jelling, This Journal, **63**, 1432 (1941).

in 10 ml. of xylene. The mixture was filtered and the filtrate was taken to dryness, giving 90 mg. of material. This material melted at 255–260° alone, at 256–261° when mixed with the iodide and at 208–240° when mixed with triptycene.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Cyclic Polyolefins. XXX. Reactions of Cycloöctatrienone; Ethoxycycloöctatetraene

BY ARTHUR C. COPE, SIDNEY F. SCHAEREN AND ELMER R. TRUMBULL[1]

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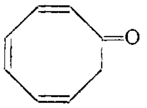
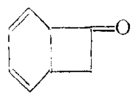
2,4,6-Cycloöctatrien-1-one (I) has been isolated as a yellow crystalline solid, m.p. 13.5–14.5°. The ketone I shows little tendency to form an enolate with bases, even though the enolate would be completely conjugated. Condensation of the ketone with ethyl cyanoacetate formed an alkylidene ester III with an exocyclic double bond. Diels–Alder adducts of the ketone I with maleic anhydride, dimethyl acetylenedicarboxylate and 1,4-naphthoquinone were prepared, and evidence is presented indicating that all of them are derived from the valence tautomer of I (formula II) containing a cyclobutanone ring. The diethyl ketal of I (formula XIV) on heating in the presence of *p*-toluenesulfonic acid or aluminum *t*-butoxide forms ethanol and ethoxycycloöctatetraene (XVI), which was characterized by hydrolysis to the ketone I and by hydrogenation to cycloöctyl ethyl ether.

This paper reports an investigation of some of the reactions of 2,4,6-cycloöctatrien-1-one (I), prepared by the base-catalyzed isomerization of cycloöctatetraene oxide.[2] The ketone was isolated as a pure liquid in 80–90% yield by distillation of the product obtained by rearrangement of cycloöctatetraene oxide. It solidified on cooling, and after recrystallization from pentane melted at 13.5–14.5°. The crystalline ketone immediately after melting had an infrared spectrum with a strong carbonyl band at 6.0μ and a weaker band at 5.63μ as previously reported, probably indicating the presence of the bridged isomer II with the carbonyl group in a four-membered ring.[2] The infrared spectrum of a single crystal of the ketone in the 5–6μ region was determined by the microspectrometric method described by Blout and Bird.[3] Both carbonyl bands present in the spectrum of the liquid ketone were present in the spectrum of the crystal, which accordingly may contain both molecular species I and II.



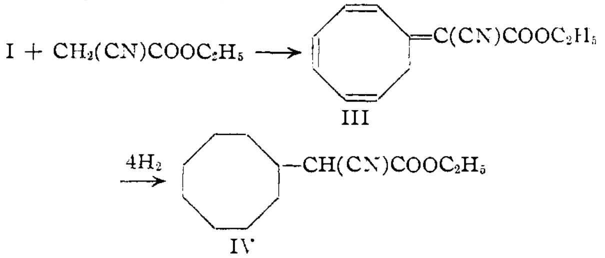
I



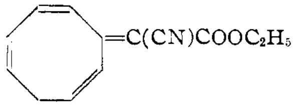
II

The ketone I does not appear to form an enolate readily. It is soluble to the extent of at least 1% in 3 *N* sodium hydroxide, but is somewhat soluble in water, and can be recovered unchanged from alkaline solution by extraction with ether. Treatment of I with sodium ethoxide in ethanol and with potassium *t*-butoxide in *t*-butyl alcohol led to decomposition, and preliminary attempts to alkylate the ketone with diethyl sulfate or ethyl iodide in the presence of these bases or sodamide in benzene were unsuccessful.

Condensation of the ketone I with ethyl cyanoacetate in the presence of ammonium acetate formed a mixture from which a yellow crystalline solid, $C_{13}H_{13}NO_2$ (III), m.p. 75–76°, was isolated in 10% yield. Quantitative hydrogenation of III in the presence of palladium on Norit resulted in absorption of four molar equivalents of hydrogen and formed a liquid octahydro derivative, $C_{13}H_{21}NO_2$ (IV). A crystalline amide prepared from IV and ammonium hydroxide proved to be identical with an authentic sample of cycloöctylcyanoacetamide, derived from ethyl cycloöctylcyanoacetate (obtained by hydrogenating ethyl cycloöctylidenecyanoacetate, prepared from cycloöctanone and ethyl cyanoacetate).



Evidence that one double bond in III is exocyclic was furnished by the ultraviolet absorption spectrum which has two strong maxima at 258 mμ (log ϵ 4.21) and 350 mμ (log ϵ 4.03) in cyclohexane, instead of the low absorption in this region characteristic of cycloöctatetraene derivatives.[4] This evidence does not exclude a cross-conjugated structure V rather than III for the ester.



V

Cycloöctatrienone reacted readily with maleic anhydride, forming a crystalline adduct VI, which was converted into the corresponding dibasic acid VII by saponification, and subsequently into the dimethyl ester VIII with diazomethane. The infrared spectrum of the dimethyl ester VIII (Fig. 1) has a strong absorption band at 5.63μ indicating that the ketonic carbonyl group is located in a four-membered ring.[5] Bridging in the

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(1) du Pont Postdoctorate Fellow.

(2) A. C. Cope and B. D. Tiffany, THIS JOURNAL, **73**, 4158 (1951).

(3) E. R. Blout and G. R. Bird, *J. Opt. Soc. Am.*, **41**, 547 (1951). We are indebted to Mr. Mario Abbate and Dr. Blout for determination of the spectrum.

(4) A. C. Cope and D. F. Rugen, *ibid.*, **75**, 3215 (1953).

(5) See J. D. Roberts and C. W. Sauer, *ibid.*, **71**, 3925 (1949), for the infrared spectrum of cyclobutanone.