THE JOURNAL OF Organic Chemistry®

VOLUME 36, NUMBER 6

MARCH 26, 1971

Conformational Analysis. LXX. The Perhydrophenanthrenes[1,2]

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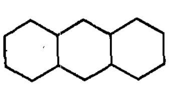
Received October 2, 1970

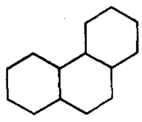
The geometries and energies of the six perhydrophenanthrenes have been calculated by the Westheimer method. Four of the isomers have been synthesized and characterized. Preliminary measurements of the composition of a perhydrophenanthrene sample equilibrated over a palladium catalyst are consistent with the structural assignments and calculated energies.

Fused ring systems have long been of interest to organic chemists, both because of their wide occurrence in the compounds of nature, and because they present challenging problems in relating chemical behavior to three-dimensional structure. Monocyclic compounds have been studied at length, and bicyclic compounds reasonably so.[5,6] Tricyclic compounds are, on the whole, not a well-studied group.[5,6]

Among the more simple (from a conformational point of view) of the tricyclic compounds are the perhydroanthracenes (PHA) and the perhydrophenanthrenes (PHP). There are five diastereoisomers of PHA, all of which are known compounds,[7] and six isomers of PHP, of which none has previously been reported in pure form.



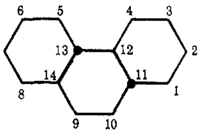
PHA



PHP

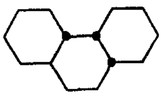
Cyclohexane is conformationally a very simple molecule, which exists essentially completely in one conformation. Decalin, which has two cyclohexane rings fused together, exists in two diastereomeric forms, cis and trans. The latter consists of a single conformation, and the former is a mixture of rapidly equilibrating enantiomers. In the PHA and PHP molecules, the isomer problem is much more complicated and was examined in some detail many years ago by Johnson[8].

The six diastereomers of PHP are shown in projection and perspective formulas, and the relative energies of each as estimated by Johnson are also shown. These energies were obtained by counting gauche interactions, and allowing 0.8 kcal/mol for each. Two of the molecules contain features for which Johnson could only guess energies: the trans-syn-trans isomer (tst) has ring B in a boat or twist-boat conformation, and the cis-syn-cis isomer (csc) contains a 1,3-syn-diaxial interaction. These features are best seen with the aid of perspective formulas.



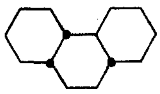
1

trans-anti-trans (tat), 0.8 kcal



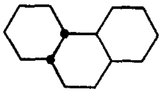
2

trans-syn-cis (tsc), 3.2 kcal



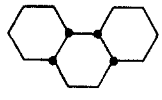
3

cis-anti-trans (cat), 3.2 kcal



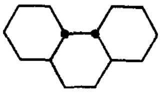
4

cis-anti-cis (cac), 4.8 kcal



5

cis-syn-cis (csc), 7.2 kcal



6

trans-syn-trans (tst), 5.6 kcal

The energy of a boat form of a cyclohexane ring, relative to a chair, was approximately known to Johnson from early work by Pitzer[9] on cyclohexane itself. The value in a related (perhydroanthracene) compound was

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[1] Paper LXIX: N. L. Allinger, M. T. Tribble, M. A. Miller, and D. H. Wertz, *J. Amer. Chem. Soc.*, in press.

[2] This work was supported in part by Public Health Service Research Grant No. AM-5836 from the National Institute of Arthritis and Metabolic Diseases.

[3] Correspondence concerning this work should be directed to this author at the University of Georgia.

[4] U. S. Public Health Service Post-Doctoral Research Fellow, 1968–1970.

[5] E. L. Eliel, N. L. Allinger, S. J. Angyal, and G. A. Morrison, "Conformational Analysis," Wiley, New York, N. Y., 1965.

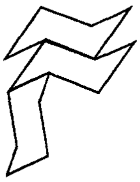
[6] E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill, New York, N. Y., 1962.

[7] R. L. Clarke, *J. Amer. Chem. Soc.*, **83**, 965 (1961).

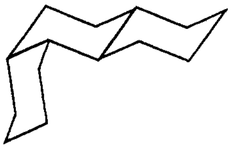
[8] W. S. Johnson, *ibid.*, **75**, 1498 (1953).

[9] C. W. Beckett, K. S. Pitzer, and R. Spitzer, *ibid.*, **69**, 2488 (1947).

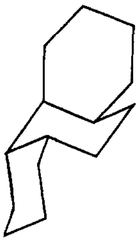
tat 1



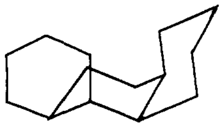
tsc 2



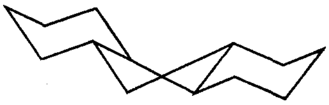
cat 3



cac 4



csc 5



tst 6

subsequently determined by heat of combustion measurements,[10] and it supports the earlier estimates.

The energy of a 1,3-syn-diaxial interaction had been guessed at by Pitzer,[11] and the value subsequently measured on methylated cyclohexanes[12] supported Pitzer's estimate.

Johnson counted one 1,3-syn-diaxial interaction of the methyl–methyl type in csc (**5**), but there are actually *two* interactions of this type. There are also seven *skew*-butane interactions, so that the estimate should have been $7 \times 0.8 + 2 \times 2.8 = 11.2$ kcal/mol. Since deformation of the ring system to relieve the syn-diaxial interactions acts in the same direction for both interactions, the ΔE value calculated by molecular mechanics is somewhat lower (9.0 kcal).

Results and Discussion

In this paper, some experimental and calculational results concerning the PHP isomers will be presented. The PHA isomers will be discussed separately later.

Calculational Work.—In previous papers we have discussed the Westheimer method for obtaining molecular geometries and energies.[1,13] This calculational method has been applied to the present problem, and the results are summarized in Table I. Data on the decalins are also included for reference purposes.

Since the calculational method is known to be quite good for hydrocarbons which are not excessively strained, the calculated values for the decalins come out in good agreement with experiment as expected. The calculated values for the perhydrophenanthrenes are thought to be similarly good, but no experimental values are available for comparison. The agreement between our detailed calculations and the estimates by Johnson is very close, except for the two isomers containing the unusual steric interactions. As we had supposed, these latter two structures give calculated energies somewhat higher than do estimates based on simple compounds, but the early estimates are pretty good. It is of interest that for tst (**6**) the B ring is found to be in a twist–boat form. The classical boat is almost 1 kcal/mol higher in energy.

TABLE I

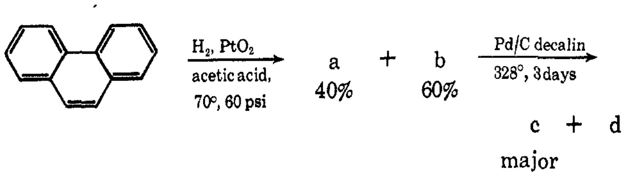
THE ENERGIES OF THE ISOMERIC PERHYDROPHENANTHRENES AND DECALINS (GAS PHASE, 25°)

Compd	$H_f°$ (calcd)	Relative enthalpies: This work	Johnson	Experimental
trans-decalin	−43.68	0.0	0.0	0
cis-decalin	−40.89	2.79	2.4	3.09 ± 0.77[a]
tat **1**	−56.03	0.0	0.0	
tsc **2**	−53.60	2.44	2.4	
cat **3**	−53.47	2.57	2.4	
cac **4**	−52.02	4.01	4.0	
csc **5**	−47.03	9.01	7.2	
tst **6**	−49.01	7.03	5.6	

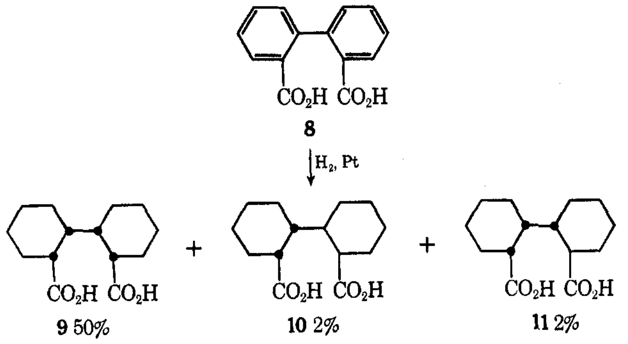
[a] D. M. Speros and F. D. Rossini, *J. Phys. Chem.*, **64**, 1723 (1960).

We wished to test the theoretical predictions experimentally and to that end have undertaken the synthesis of the isomeric perhydrophenanthrenes. In this paper are reported the syntheses and structure proofs of four of the six isomers. We hope to report on the remaining two isomers at a later date.

Experimental Work.—A reasonable starting place appeared to be the hydrogenation of phenanthrene itself.[14] When phenanthrene was hydrogenated with the aid of a platinum catalyst, there were formed two isomers, a (40%) and b (60%), as established by vpc.



Diphenic acid (**8**) has been observed to give the products shown under similar conditions.[15] In view of these re-



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[10] J. L. Margrave, M. A. Frisch, R. G. Bautista, R. L. Clarke, and W. S. Johnson, *J. Amer. Chem. Soc.*, **85**, 546 (1963).

[11] C. W. Beckett, K. S. Pitzer, and R. S. Spitzer, *ibid.*, **69**, 2488 (1947).

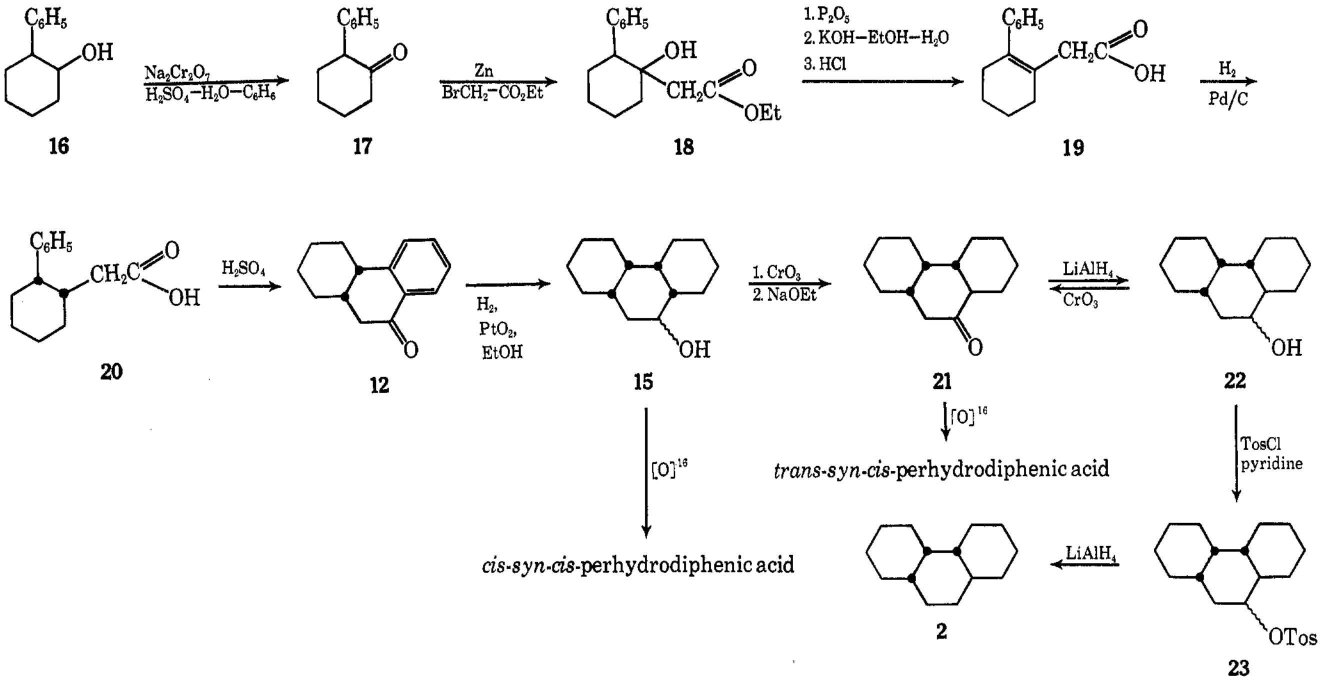
[12] N. L. Allinger and M. A. Miller, *ibid.*, **83**, 2145 (1961).

[13] (a) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **91**, 337 (1969); (b) N. L. Allinger, J. A. Hirsch, M. A. Miller, and I. J. Tyminski, *ibid.*, **90**, 5773 (1968); (c) N. L. Allinger, J. A. Hirsch, M. A. Miller, I. J. Tyminski, and F. A. Van-Catledge, *ibid.*, **90**, 1199 (1968); (d) N. L. Allinger, M. A. Miller, F. A. Van-Catledge, and J. A. Hirsch, *ibid.*, **89**, 4345 (1967).

[14] We have been able to carry out this reaction in the Parr low pressure apparatus. The following workers have studied the conditions of high pressure hydrogenation of phenanthrene, but not with the intent of identifying the resulting isomers: (a) I. Kagehira, *Bull. Chem. Soc. Jap.*, **6**, 241 (1931); (b) J. R. Durland and H. Adkins, *J. Amer. Chem. Soc.*, **59**, 135 (1937).

[15] R. P. Linstead, W. v. E. Doering, S. B. Davies, P. Levine, and R. R. Whetstone, *ibid.*, **64**, 1985 (1942).

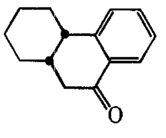
SCHEME I



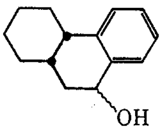
sults, as well as the expected cis addition by hydrogen, it was thought that the hydrogenated phenanthrenes, a and b, should correspond to materials with these largely cis-stereochemical backbones.

Preliminary investigation also included the equilibration of the mixture, a and b, over a Pd/C catalyst, whereby there were produced two isomers, c and d, with c constituting about 80% of the mixture. Some material with the same retention time as a remained, although b seemed to have completely disappeared. In light of these results and previously mentioned considerations, it was concluded that b, the major isomer from the hydrogenation of phenanthrene, was **5**, the all-cis isomer, and a was either **2** or **4**, analogous to the case of the perhydrodiphenic acids. Compound c, produced by equilibration, was almost certainly **1**, the most stable all-trans isomer; d, also produced in the equilibration, could be either **2** or **3**, the next most stable of the isomers.

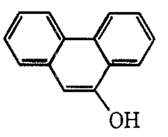
It has been said that b must be **5**. Further evidence supports this assignment. When the related compounds **12**, **13**, or **14** were hydrogenated, the same hydrocarbon mixture of a and b was obtained. The products from *cis*-9-ketooctahydrophenanthrene (**12**), *cis*-octahydro-9-phananthrol (**13**), and 9-phenanthrol (**14**) all gave the same two peaks on vpc with b accounting for 80, 80, and 53% of the mixture, respectively.



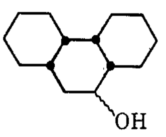
12



13



14



15

The hydrogenation of **12** was of particular value, as there was also isolated (in addition to a and b) the known solid *cis-syn-cis*-9-perhydrophenanthrol (**15**). With b now assigned as isomer **5**, it was separated by preparative vpc and may be obtained readily in this manner. Next, isomer a was shown to be **2**, *trans-syn-cis*-perhydrophenanthrene, as it was identical with the compound obtained from Scheme I.

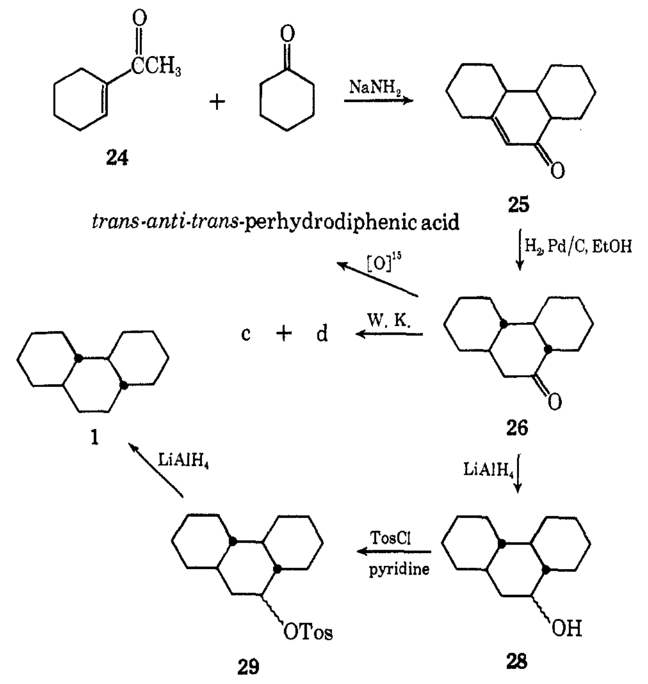
Although the scheme to **22** has been reported previously,[16] enough anomaly was encountered to warrant its inclusion here (see Experimental Section). The stereochemical integrities of **15** and **22** have been demonstrated by oxidation to the respective known perhydrodiphenic acids.[16] Conversion of **22** to the trans-syn-cis isomer **2**, proceeded *via* reduction of the tosylate **23**, and the resulting pure liquid material corresponded in all respects to a (vpc, refractive index, nmr).

Attention was then focused on c, thought to be the trans-anti-trans isomer **1**, and indeed this was shown to be the case when the material from Scheme II proved to be identical with c. The *trans-anti-trans*-9-ketoperhydrophenanthrene (**26**) was prepared essentially by the method of Rapson and Robinson.[17] Proof of structure was *via* oxidation to the known perhydrodiphenic acid. Initially an attempt was made to reduce the carbonyl *via* some direct route; however, this proved to be unsatisfactory for complete and unambiguous conversion to a single isomer. Wolf–Kishner reduction, for example, gave two peaks c and d, with c predominating. Since these materials arose from the known trans-anti-trans precursors, it is logical that c should be the trans-anti-trans isomer (product of either thermodynamic or kinetic control), and this was proven later. If this proof is anticipated for the moment, d can only be the trans-anti-cis isomer **3**, arising from epimerization (by either acid or base catalysis) of the center adjacent to the carbonyl, followed by reduction of the resulting ketone. The isomeric hydrocarbon pair c and d could not be

[16] R. P. Linstead and R. R. Whetstone, *J. Chem. Soc.*, 1428 (1950).

[17] W. S. Rapson and R. Robinson, *ibid.*, 1285 (1935).

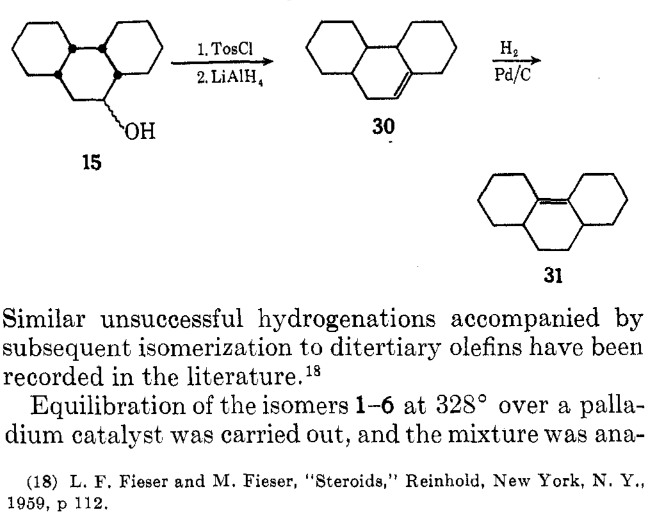
SCHEME II



effectively separated preparatively, and hence d or **3** was not studied further.

Final proof of the identity of c was by way of the tosylate **29** and reduction to a single pure liquid. This material must be *trans-anti-trans*-perhydrophenanthrene (**1**); it was identical with c as judged by vpc, nmr, and refractive index.

Finally, although b has been clearly shown to be **5**, an attempt was also made to prepare it from **15**. The tosylate route now was no longer successful, since **15** could not be completely converted to a tosylate. The infrared spectrum indicated that a mixture of alcohol and tosylate was obtained (despite repeated attempts, the pure tosylate could not be isolated). Reduction of the mixture that was obtained did give material with retention time of b, but this was an olefin as demonstrated by bromine in chloroform and tetranitromethane tests, as well as analysis and nmr. Attempted hydrogenation changed this olefin to material with retention time of a; this was also olefinic. The absence of vinyl hydrogen absorption in the nmr spectrum of the latter olefin suggests that it was the ditertiary olefin **31**. The material still reacted readily with bromine in chloroform.



Similar unsuccessful hydrogenations accompanied by subsequent isomerization to ditertiary olefins have been recorded in the literature.[18]

Equilibration of the isomers **1–6** at 328° over a palladium catalyst was carried out, and the mixture was analyzed by vpc. It was not possible to accurately establish the free-energy differences in this way. The separations were not clean, and it was only possible to measure the composition of the mixture approximately as follows: **1** (85%), **2** (10%), **3** (5%), **4**, **6** (not detected), **5** (less than 0.5%). While of very limited accuracy, these values are consistent with the structural assignments and calculated energies.

Experimental Section[19]

Infrared spectra were recorded with a Beckman Model IR-4 spectrophotometer. Nmr spectra were taken on a Varian A-60 spectrometer; chemical shifts are relative to internal TMS = 0 ppm. The two columns used for vpc analyses were 0.25 in. o.d. × 10 ft 5% silicone oil on firebrick (column A) and 0.25 in. o.d. × 6 ft 10% polyglycol on firebrick (column B).

Hydrogenation of Phenanthrene.—A solution of 25 g of phenanthrene in 200 ml of acetic acid was hydrogenated in the presence of 3 g of platinum oxide catalyst at 70° and an initial pressure of 60 psig. Since very little hydrogen was taken up in the first 3 days, the catalyst was removed by filtration and a fresh 3-g portion was added. Hydrogenation under the same conditions then proceeded at a reasonable rate. After the theoretical amount of hydrogen had been taken up, the mixture was allowed to remain under these conditions 1 day more. The solution was cooled and the catalyst was again removed. The solvent was removed with the use of an aspirator while heating on the steam bath. The remaining oil was taken up in pentane, washed with sodium carbonate solution and water, and dried, and the solvent was removed. The residue was distilled *in vacuo* to give 19 g (80%) of a main fraction, bp 119–125° (4 mm). This product gave a positive (yellow) tetranitromethane test and showed two main vpc peaks on column A at 200° and 7 psig. A shoulder peak (a) was immediately followed by the main peak (b). If the temperature and pressure were lowered, the first peak (a) gave indications of a third component. These two isomeric compounds were later identified as the cis-syn-cis isomer **5** (peak b), which comprised 60% of the mixture, and the trans-syn-cis isomer **2** (peak a) present to the extent of 40%. The mixture had $n^{25}\text{D}$ 1.5084.

Equilibration of the Perhydrophenanthrenes.—A solution of 10 g of the perhydrophenanthrene mixture from the hydrogenation of phenanthrene (40% tst, 60% csc) in 20 g of decalin, together with 1.5 g of palladium on charcoal, was allowed to stand for 3 days in a sealed tube at 328°. Vpc analysis of the resulting material showed it to contain roughly 85% *trans-anti-trans-*, 5% *cis-anti-trans-*, and 10% *trans-syn-cis*-perhydrophenanthrene. The separations were not clean, and more accurate analyses will have to await the availability of more efficient equipment.

***cis-syn-cis*-Perhydrophenanthrene** (**5**).—Isolation of the main product from hydrogenation of phenanthrene (b) by preparative vpc gave a liquid which gave a negative tetranitromethane test and showed now only one vpc peak. This material has been assigned the cis-syn-cis structure. The nmr confirmed that no olefinic material was present, and the material had $n^{25}\text{D}$ 1.5120.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.28; H, 12.58.

***trans*-Δ¹⁰-9-Ketododecahydrophenanthrene** (**25**).—To a stirred, cooled slurry of 30 g of sodium amide in 1 l. of anhydrous ether, a solution of 75 g of cyclohexanone in 500 ml of ether was added over a period of 1 hr. After an additional 0.5 hr, a solution of 88 g of freshly distilled acetylcyclohexene was added over a period of 3 hr. Overnight stirring at room temperature was followed by the cautious addition of 500 ml of water. The ether layer was separated, washed with water, and dried, and the solvent was removed. The oily residue was distilled to give a forerun, bp 65–154° (3 mm), followed by the product, bp 154–160° (3.5 mm). This fraction soon solidified and was recrystallized from ether to give 30 g (29%, based on recovered cyclohexanone) of the product, mp 85–90° (reported[20] mp 87–88°).

***trans-anti-trans*-Perhydro-9-phenanthrol** (**28**).—Reduction of the α,β-unsaturated ketone **25** to the saturated ketone **26** (mp 48–50°) with hydrogen and a palladium catalyst, followed by

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[18] L. F. Fieser and M. Fieser, "Steroids," Reinhold, New York, N. Y., 1959, p 112.

[19] The authors are indebted to Drs. L. A. Tushaus and A. R. Perry for some preliminary experiments on this problem.

[20] R. P. Linstead and A. L. Walpole, *J. Chem. Soc.*, 842 (1939).

lithium aluminum hydride reduction, gave the alcohol **28**, mp 118.5–120° (reported[20] mp 119°).

trans-anti-trans-**Perhydrophenanthrene-9-*p*-toluenesulfonate (29).**—To a stirred solution of 3.1 g of *trans-anti-trans*-perhydro-9-phenanthrol (**28**) in 20 ml of dry pyridine was added a solution of 3.42 g of *p*-toluenesulfonyl chloride in 8 ml of pyridine over a period of 0.5 hr at room temperature. After stirring for 2 hr, the mixture was allowed to stand overnight. Ice was added and the solution was allowed to stand for 1 hr. Concentrated hydrochloric acid was added followed by additional ice, and the solution was allowed to stand 1 hr more. The ether layer was separated and the aqueous layer was extracted with additional ether. The combined ether layers were washed with sodium carbonate solution and water and dried, and the solvent was removed. At this point, 25 ml of ether and 25 ml of 95% ethanol were added, and the material was crystallized in a Dry Ice–acetone bath. The solid was recrystallized three times in this manner to give 1.8 g (33%) of the product, which softened at 94° and melted at 108.5–110°. The infrared spectrum showed bands at 7.9, 8.4, and 8.5 μ characteristic of a tosylate.

Anal. Calcd for $C_{21}H_{30}O_3S$: C, 69.57; H, 8.39. Found: C, 69.48; H, 8.54.

trans-anti-trans-**Perhydrophenanthrene (1).**—To a stirred solution of 2 g of lithium aluminum hydride in 100 ml of ether, a solution of 1.75 g of tosylate **29** in 25 ml of ether was added during a period of 0.5 hr. Stirring was discontinued 2 hr after the addition was complete, and the solution was allowed to stand overnight. Water was added, followed by 10% hydrochloric acid. The solution was then washed with sodium carbonate solution and water and dried, and the solvent was removed. The remaining yellow oil was taken up in the minimum amount of pentane and chromatographed on 8 g of neutral activity I Woelm alumina. The first fraction contained 200 mg (21%) of the product, mp 18–19° (no other material was detected in later fractions). The compound gave a negative TNM test; vpc showed one peak on column A at 200° and 7 psig, $n^{25}\text{D}$ 1.4942. The nmr spectrum also showed the absence of olefinic material.

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.67; H, 12.46.

Wolff–Kischner Reduction of *trans-anti-trans*-9-Ketoperhydrophenanthrene (26).—A solution of 2.5 g of *trans-anti-trans*-9-ketoperhydrophenanthrene (**26**), 4.5 g of 85% hydrazine hydrate, and 5 g of sodium hydroxide in 50 ml of redistilled diethylene glycol was heated until the temperature in the reaction flask reached 150°. This temperature was maintained for 1.5 hr to allow the completion of hydrazone formation. The temperature was gradually increased to distil excess hydrazine and water from the reaction vessel, until the temperature of the mixture had reached 225°. This temperature was maintained for 4 hr. After the mixture had cooled, it was extracted with pentane; the extract was washed with water and dried. The ether solution was concentrated to a small volume and chromatographed on A-540 Fisher alumina. From the first fractions was obtained an oil which gave a negative TNM test. The material gave one main peak with a shoulder on vapor phase chromatography on column A at 198° and 8 psig; the resolution was worse on column B at 146° and 5 psig. The major peak had the same retention time as the previously described trans-anti-trans isomer prepared by the reduction of the corresponding tosylate. On column A, the two peaks again were identical with the two major peaks (a and b) from the hydrogenation of phenanthrene. Since the material gave a completely negative TNM test, the shoulder peak must be the cis-anti-trans isomer **3**, an isomer which was not obtained by other means.

cis-**9-Keto-1,2,3,4,9,10,11,12-octahydrophenanthrene (12).**—2-Phenylcyclohexanol (Aldrich) was oxidized with dichromate to 2-phenylcyclohexanone, mp 58–60° (reported mp 50–53°,[21] 53–55°[22]), which underwent a Reformatsky reaction with ethyl bromoacetate and zinc to give ethyl 2-phenylcyclohexanol-1-acetate, bp 155–175° (4 mm) [reported[21] bp 146–154° (0.8 mm)]. Dehydration of this material with phosphorus pentoxide gave the unsaturated ester, bp 144–154° (3 mm) [lit. bp 123–125° (0.8 mm),[21] 146–153° (3 mm)[23]]. The latter was saponified with potassium hydroxide and gave 2-phenyl-Δ^1-cyclohexenylacetic acid (**19**) as a gum, bp 165–180° (1.5 mm) [lit. bp 150–155° (0.4 mm),[21] 180–190° (3 mm)[23]]. Hydrogenation of this compound with palladium on carbon in acetic acid gave *cis*-2-phenylcyclohexaneacetic acid (**20**), mp 165–170° (lit.[21,23] mp 168–170°).

To 11 g of *cis*-2-phenylcyclohexaneacetic acid (**20**), 55 g of concentrated sulfuric acid was added in one portion. The mixture was heated on a steam bath with occasional swirling for 15 min and then poured directly onto ice. The resulting milky solution was allowed to come to room temperature and was extracted with ether. The ether layer was washed with sodium carbonate solution and water and dried, and the solvent was removed. The resulting yellow oil was distilled to give 8.7 g (86%) of the product, bp 155–157° (2 mm) [lit. bp 132–135° (0.5 mm),[21] 162–163° (5 mm)[23]].

cis-syn-cis-**Perhydro-9-phenanthrol (15).**—The hydrogenation of a solution of 13.4 g of **12** in 60 ml of ethanol was carried out on the presence of 0.5 g of platinum oxide at room temperature and an initial pressure of 39 psig. Six days were required for the the theoretical amount of hydrogen to be taken up. During this time two more 0.25-g portions of catalyst were added so that the total amount of catalyst used was 1 g. At the end of this time the solution was filtered through Celite, and the solvent was removed with the use of an aspirator. The resulting oil was dissolved in hexane and cooled to give 6 g of material having mp 80–100° (lit.[24] mp 70–85°). This material did not crystallize readily and was best separated by first cooling in a Dry Ice–acetone bath thoroughly and then slowly warming in a beaker of water. Recrystallization from cyclohexane gave 5.0 g (36)% of material of mp 108–110° (lit.[24] mp 108–110°). The infrared spectrum was characteristic of an alcohol. The perhydrophenanthrene residue which was obtained from the hexane mother liquor showed 20% a and 80% b by vpc.

Attempt to Synthesize *cis-syn-cis*-Perhydrophenanthrene from *cis-syn-cis*-9-Perhydrophenanthrol (15). A. Tosylation of *cis-syn-cis*-9-Perhydrophenanthrol (15).—To a stirred solution of 1.9 g of *cis-syn-cis*-perhydro-9-phenanthrol (**15**) in 15 ml of dry pyridine, a solution of 2.86 g of *p*-toluenesulfonyl chloride in 5 ml of pyridine was added at room temperature over a period of 0.5 hr. Stirring was continued for 3 hr and the resulting solution was allowed to stand for 3 days. At the end of this time an excess of ice was added, followed by 10 ml of concentrated hydrochloric acid. After the mixture was allowed to stand for 2 hr, it was extracted with ether. The ether layer was washed with sodium carbonate solution and water and dried, and the solvent was removed. Attempted crystallization of the resulting oil from ether–95% ethanol at −78° was unsuccessful. Although a small amount of solid material separated, most of the material remained as an oil. The infrared spectrum of this oil showed absorption at 2.9, 7.9, and 8.5 μ, indicating a mixture of starting alcohol and tosylate. This was used directly in the next step.

B. Reduction of Tosylate Mixture.—To a stirred solution of 0.75 g of lithium aluminum hydride in 30 ml of ether, a solution of the previously described oil from the tosylation of 0.9 g of **15** in 20 ml of ether was added over a period of 0.5 hr. After 3 hr of additional stirring, the solution was allowed to stand at room temperature for 3 days. Water was added, followed by 75 ml of 10% hydrochloric acid solution. The ether layer was separated and the aqueous layer was extracted with additional ether. The combined ether extracts were washed with water and dried, and the solvent was removed. The remaining oil was taken up in pentane and chromatographed on 5 g of neutral activity I Woelm alumina. From the first fraction was obtained 400 mg (52%) of a clear liquid, which had $n^{25}\text{D}$ 1.5115. The product gave a positive (yellow) TNM test. The vpc retention time (column A at 200° and 7 psig) was identical with that of isomer b from the hydrogenation of phenanthrene. The uptake of the peak showed some distortion. The nmr spectrum showed vinyl proton absorption at τ 4.8. The nmr spectrum and the infrared spectrum, which had strong bands at 11.7–12.5 μ characteristic of a trisubstituted olefin, suggest structure **30**. It was calculated from the nmr spectrum that about 83% of the material was compound **30**.

Anal. Calcd for $C_{14}H_{22}$: C, 88.36; H, 11.80. Found: C, 88.30; H, 11.80.

C. Atttempted Hydrogenation of Olefin 30 from the Reduction of the Tosylate Mixture from *cis-syn-cis*-9-Perhydrophenanthrol

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[21] J. W. Cook, C. L. Hewett, and C. A. Lawrence, *J. Chem. Soc.*, 71 (1936).

[22] C. C. Price and J. V. Karabinos, *J. Amer. Chem. Soc.*, **62**, 1159 (1940).

[23] R. P. Linstead, R. R. Whetstone, and P. Levine, *ibid.*, **64**, 2014 (1942).

[24] R. P. Linstead, R. R. Whetstone, and P. Levine, *ibid.*, **64**, 2014 (1942).

(**15**).—A mixture of 240 mg of olefin **30**, 56 mg of 10% Pd/C catalyst, and 10 ml of ethanol showed hardly any uptake of hydrogen after 2 hr at atmospheric pressure. Removal of the catalyst and solvent gave a material which had $n^{25}\mathrm{D}$ 1.501. Although the nmr spectrum revealed that the vinyl protons were now completely gone, the material readily reacted with an excess of a 2% bromine in chloroform solution (the mixture of a and b from the hydrogenation of phenanthrene did not), and gave a strong (brown) TNM test. These results indicate that an olefin such as **31** was formed which is resistant to hydrogenation.

***cis-as*-Octahydro-9-phenanthrol (13). A. Lithium Aluminum Hydride Reduction of Ketone.**—Reduction of 5 g of *cis*-octahydro-9-ketophenanthrene (**12**) with lithium aluminum hydride in ether solution was followed by acidic work-up. Recrystallization of the product from cyclohexane gave 4.3 g (84%) of **13**, mp 114–116° (reported mp 115–116°,[24] 114–115°[21]).

B. Hydrogenation of the Ketone.—A mixture of 9.55 g of *cis*-octahydro-9-ketophenanthrene (**12**) and 4.15 g of slightly impure *cis-as*-octahydro-9-phenanthrol (**13**) was dissolved in 75 ml of ethanol and hydrogenated in the presence of 0.75 g of platinum oxide catalyst. The reaction was complete after 4 days at room temperature and 30–50 psig. The catalyst was removed by filtration and the solvent was removed with the use of an aspirator. The resulting material was recrystallized twice from cyclohexane to give 13 g of crystals, mp 108–113° (lit. 115–116°,[24] 114–115° [21]).

Hydrogenation of *cis-as*-Octahydro-9-phenanthrol (13). A. In Ethanol–Platinum Oxide.—One gram of **13** was dissolved in 35 ml of ethanol and 1.5 ml of acetic acid and hydrogenated at room temperature and 30 psig in the presence of 0.25 g of platinum oxide catalyst. After 3 days, hydrogen uptake became slow. Removal of the catalyst and solvent gave an oil which was taken up in ether. The ether solution was washed with water and dried, and the solvent was removed. The resulting oil showed two vpc peaks on column A at 109° and 9 psig which were identical in retention time with those observed for the products of hydrogenation of phenanthrene and of 9-phenanthrol (a and b). In this case, the second peak (b) (the cis-syn-cis isomer, **5**) comprised about 80% of the mixture.

B. In Ethanol–Rhodium/Alumina.—Hydrogenation of a solution of 1.85 g of the alcohol in 20 ml of methanol and 1.5 ml of acetic acid in the presence of 2.5 g of rhodium-on-alumina catalyst, under the conditions described above, gave the same two isomers (a and b), together with the starting alcohol. Since this hydrogenation did not proceed well and did not go to completion, it was not pursued further.

Hydrogenation of 9-Phenanthrol (14). A. With Platinum Oxide in Acetic Acid.—To a solution of 11 g of 9-phenanthrol (**14**) in 100 ml of ether, Norit was added. After the solution was allowed to stand for 2 hr, it was filtered, and 1 teaspoon of W-2 Raney nickel was added. After standing again for 2 hr, the solution was filtered through Celite and the solvent was removed. The solid now had mp 151–153° (lit.[25] 153–155°) and started to take on a color; it was immediately taken up in 200 ml of acetic acid and hydrogenated in the presence of 2 g of platinum oxide catalyst at an initial pressure of 40 psig. The theoretical amount of hydrogen was taken up in 24 hr. After filtration through Celite, 200 ml of water was added and the solution was extracted with ether. The ether solution was washed with water and dried, and the solvent was removed. The resulting oil, which solidified upon standing overnight, was taken up in the minimum amount of pentane–benzene and chromatographed on 322 g of neutral activity I Woelm alumina. Fractions of 200 ml were taken and the following series of solvents was used: 50, then 75% benzene–pentane; benzene; 1, 5, 10, 25, and 50% ether–benzene; ether; 1, 5, and 10% methanol–ether. The second fraction was found by vpc (column A at 210° and 7 psig) to contain the same two isomers (a and b) obtained from the hydrogenation of phenanthrene, in the ratio of about 53% b (cis-syn-cis) to 47% a (trans-syn-cis). The latter fractions contained an oil which solidified upon standing. Two recrystallizations from Norit-treated hexane solutions gave 1 g of sym-octahydro-9-phenanthrol, mp 133–135° (lit.[24] 134–135°).

***trans-syn-cis*-Perhydrophenanthrene-9-*p*-toluenesulfonate (23). A. *cis-syn-cis*-9-Ketoperhydrophenanthrene.**—To a stirred solution of 1.5 g of *cis-syn-cis*-9-perhydrophenanthrol (**15**) in 25 ml of acetone, Jones reagent was added until the orange color of the reagent remained. After stirring for 5 min, isopropyl alcohol was added to decompose the excess reagent. The resulting solution was filtered through Celite, and ether was added. The ether solution was washed with water and dried, and the solvent was removed. The absence of hydroxyl absorption and the presence of a strong carbonyl band at 5.8 μ in the infrared spectrum of the resulting oil demonstrated that the oxidation was complete. The oil was crystallized from petroleum ether at −78° to give 1 g (71%) of solid material, mp 39–41.5° (reported[24] mp 43–44°).

B. *trans-syn-cis*-9-Ketoperhydrophenanthrene (21).—A mixture of 1 g of the cis-syn-cis ketone and 25 ml of 0.75 *M* sodium ethoxide soluion was heated to reflux for 3 hr, cooled, and allowed to stand at room temperature overnight. Ether was then added to the solution, which had turned dark brown. The ether solution was washed with water and dried, and the solvent was removed. The resulting material was recrystallized from petroleum ether (after standing overnight with Norit) at −78° to give 0.5 g (50%) of the product, mp 51.5–55° (lit.[24] mp 56.5–57.5°). The infrared spectrum (CCl_4) of the crystalline material was very similar to the spectrum of the cis-syn-cis ketone. However, the melting point of a mixture of the two ketones was depressed to 24–35°.

C. *trans-syn-cis*-Perhydro-9-phenanthrol (22).—A solution of 0.5 g of *trans-syn-cis*-9-keto-perhydrophenanthrene (**21**) in 15 ml of ether was added during 2 min to a stirred slurry of 0.5 g of lithium aluminum hydride in 25 ml of ether. Stirring was continued for 2.5 hr, after which the mixture was allowed to stand overnight. Water was added, followed by 10% hydrochloric acid. The ether layer was separated, the aqueous layer was thoroughly extracted with ether, the combined ether layers were washed with water and dried, and the solvent was removed. The residue was difficult to crystallize but could be obtained as a crude solid by removing all of the solvent. The material in this state softened at 62° and melted at 69–76°. The infrared spectrum showed strong hydroxyl absorption at 2.9 μ and no carbonyl absorption and was similar to that of the cis-syn-cis alcohol (**15**) except for the presence of an additional band at 7.9 μ. Thin layer chromatography showed the crude material to contain essentially one compound, and to be different from the cis-syn-cis alcohol (**15**) which was not eluted so fast by ether. Recrystallization of the crude material from petroleum ether at −78° (requires 20–30 min to separate) gave 0.3 g (60%) of the product, mp 91–94° (lit.[24] mp 88–89°). The melting point of a mixture of this material with the cis-syn-cis alcohol (**15**) was depressed to 74–88°. The material was thus proven to be totally different and not an epimer of the starting cis-syn-cis alcohol (**15**) by this sequence.

D. *trans-syn-cis*-Perhydrophenanthrene-9-*p*-toluenesulfonate (23).—A solution of 1 g of *p*-toluenesulfonyl chloride in 3 ml of dry pyridine was added during 15 min to a stirred solution of 0.3 g of *trans-syn-cis*-9-phenanthrol (**22**) in 8 ml of pyridine. The mixture was stirred for 3 hr and then allowed to stand at room temperature overnight. Excess ice was added and the mixture was allowed to stand for 2 hr. It was then taken up in ether; the ether solution was washed with sodium carbonate solution and water and dried. Removal of the solvent gave an oil which was recrystallized twice from hexane to give 0.3 g (60%) of the product, mp 103–104.5°. The infrared spectrum showed strong bands at 7.9 and 8.5 μ characteristic of a tosylate.

The melting point of a mixture with the *trans-anti-trans*-perhydrophenanthrene-9-*p*-toluenesulfonate (**29**) (mp 101–103°) was depressed to 85–96°.

Anal. Calcd for $C_{21}H_{30}O_3S$: C, 69.57; H, 8.39. Found: C, 69.63; H, 8.34.

***trans-syn-cis*-Perhydrophenanthrene (2). A. Reduction of Tosylate (23).**—A solution of 0.65 g of *trans-syn-cis*-phenanthrene-9-*p*-toluenesulfonate (**23**) in 15 ml of ether was added during 15 min to a stirred solution of 1 g of lithium aluminum hydride in 35 ml of ether. After 2 hr of additional stirring, the solution was allowed to stand at room temperature overnight. Water was added carefully, followed by 10% hydrochloric acid. The ether layer was separated, washed with sodium carbonate solution and water, and dried. Removal of the solvent gave an oil which was chromatographed on 12 g of neutral activity I Woelm alumina in pentane. The first fraction gave an oil, $n^{25}\mathrm{D}$ 1.5015, which still gave a positive (yellow) TNM test. This material showed a single vpc peak (column A at 200° and 7 psig) of the same retention time as the first isomer (peak a) in the hydrogenation of phenanthrene. Peak a was therefore assigned to the trans-syn-cis isomer (**2**). The nmr spectrum revealed the absence of olefinic material.

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[25] L. F. Fieser, R. P. Jacobsen, and C. C. Price, *J. Amer. Chem. Soc.*, **58**, 2163 (1936).

Anal. Calcd for $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.45; H, 12.39.

B. From the Hydrogenation of Phenanthrene.—Separation of the first (a) of the two isomers obtained from the hydrogenation of phenanthrene by preparative vpc gave a product which was identical by its vpc retention time, index of refraction, and nmr spectrum with that obtained from the reduction of the tosylate **23**. After separation by vpc, this isomer was chromatographed on 5 g of neutral, activity I Woelm alumina in pentane. The material obtained gave a negative TNM test and had n^{25}_{D} 1.5015.

Anal. Calcd $C_{14}H_{24}$: C, 87.42; H, 12.58. Found: C, 87.37; H, 12.78.

Registry No.—**1**, 2108-89-6; **2**, 27425-35-0; **3**, 27389-73-7; **4**, 27389-74-8; **5**, 26634-41-3; **6**, 27389-76-0; **23**, 27389-77-1; **29**, 27389-78-2; **30**, 27389-79-3.

Studies of Acenaphthene Derivatives. XXI.[1]
Reaction of 2-Diazoacenaphthenone with Olefins and Acetylenes

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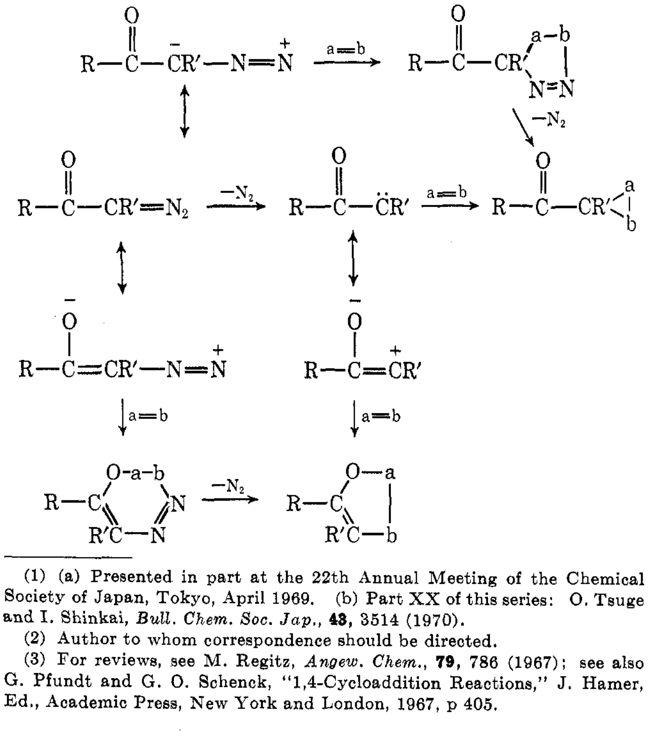
Received July 20, 1970

No thermal decomposition of 2-diazoacenaphthenone (**1**) occurred in boiling benzene or toluene for a long while. Copper-catalyzed thermolysis of **1** in boiling toluene led to the formation of biacenedione, although **1** was not decomposed in boiling benzene under the influence of copper powder. On the other hand, thermolysis of **1** in boiling xylene gave biacenedione, together with a trace amount of acenaphthenequinone ketazine. Reactions of **1** with ethyl acrylate (**2a**), acrylonitrile (**2b**), ethyl α-bromoacrylate (**2c**), methyl vinyl ketone (**2d**), and diethyl fumarate and maleate in refluxing benzene gave the corresponding spiro[acenaphthenone-2,1'-cyclopropanes] (**3a–d**, **4a–c**, **7**); with **2a**, **2b**, and **2c**, two stereoisomers obtained respectively. Although **1** did not react with cyclohexene and indene, the reaction with bicyclo[2.2.1]hept-5-ene-2,3-dicarboxylic anhydride gave the spiro-[acenaphthenone-2,3'-tricyclooctanedicarboxylic anhydride] (**8**). However, **1** reacted with acrolein to give two isomers of 2'-hydroxymethylspiro[acenaphthenone-2,1'-cyclopropanes] (**5**, **6**) corresponding to dihydro derivatives of the expected 2'-formyl compounds. On the other hand, addition of **1** to phenylacetylene and to diethyl acetylenedicarboxylate gave the corresponding spiro[acenaphthenone-2,3'(3'H)-pyrazoles] (**9**, **10**).

The thermal and photochemical reactions of α-diazo ketones, such as diazoacetophenone, azibenzil, and *o*-benzoquinone diazide, have received considerable attention.[3] Although α-diazo ketones exhibit a different behavior depending on their nature and reaction conditions, the reaction can be classified into three categories from a viewpoint of the cycloaddition, as illustrated in Scheme I. Little attention has been paid to the reaction of α-diazo ketone with olefins under such conditions that the ketocarbene is not generated, although the low temperature reactions of diazomethanes have been investigated considerably.

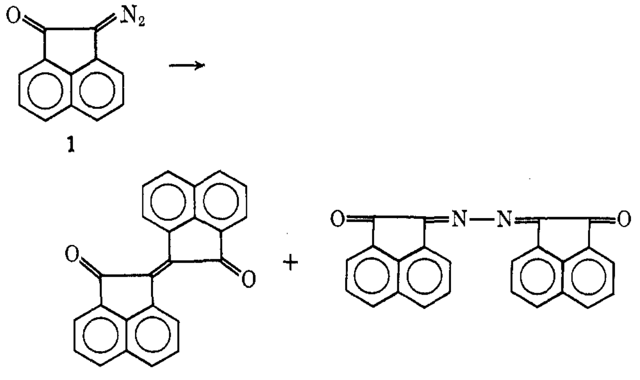
SCHEME I



In order to clarify whether 2-diazoacenaphthenone (**1**) reacts with an olefin to lead to the spiropyrazoline or -cyclopropane ring formation, or to give the dihydro-1,4,5-oxadiazepine or dihydrofuran, the reaction of **1** with various olefins in refluxing benzene has been investigated. Also, this paper deals with the reaction of **1** with acetylenes.

Results and Discussion

The diazo ketone **1** was not decomposed in boiling benzene or toluene for a long while; **1** was recovered quantitatively. Thermolysis of **1** in boiling toluene



1

was greatly accelerated by copper powder and led to the formation of diacenaphthylidenedione (biacenedione), although the decomposition of **1** did not take place in the presence of copper powder in boiling benzene. As shown by Ried and Lohwasser,[4] thermolysis of **1** in boiling xylene gave biacenedione as the main product, accompanied by a trace amount of acenaphthenequinone

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[1] (a) Presented in part at the 22th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1969. (b) Part XX of this series: O. Tsuge and I. Shinkai, *Bull. Chem. Soc. Jap.*, **43**, 3514 (1970).

[2] Author to whom correspondence should be directed.

[3] For reviews, see M. Regitz, *Angew. Chem.*, **79**, 786 (1967); see also G. Pfundt and G. O. Schenck, "1,4-Cycloaddition Reactions," J. Hamer, Ed., Academic Press, New York and London, 1967, p 405.

[4] W. Ried and H. Lohwasser, *Justus Liebigs Ann. Chem.*, **683**, 118 (1965).