by the infrared spectra of these samples. A perceptible amide band was present after 10 minutes, and the spectra indicated that the reaction essentially was complete at the end of 3 hours. After 24 hours, the spectrum was identical with that of an authentic specimen of oxyhydrastinine.[18] At that time the manganese dioxide was removed by filtration and washed twice with chloroform. The chloroform solution was washed three times with dilute hydrochloric acid and concentrated to give a solid which was recrystallized from cyclohexane, 86 mg., m.p. 96–98° (reported[18] for oxyhydrastinine 97–98°). A mixed melting point with an authentic sample, m.p. 97–98°, showed no depression. The acid solution gave 37 mg. of crude unreacted hydrastinine, m.p. 87–96°, identical in its infrared spectrum with the starting hydrastinine. The yield of oxyhydrastinine was 76% based on the starting material consumed and the removal of 11 aliquots.

2-Hydroxypyran.—A solution of 1 mmole of 2-hydroxytetrahydropyran[19] in 20 ml. of chloroform was stirred with 1.0 g. of manganese dioxide at room temperature for 24 hours. Samples of 1-milliliter volume were withdrawn at 0, 75 and 1275 minutes. A moderately strong lactone band at 5.78 μ was found after the reaction had run 75 minutes. At the end of 1275 minutes the band at 5.78 μ was very strong. The hydroxyl band at 2.95 μ showed a concurrent decrease in intensity but still was present at the end of the reaction. The reaction product gave a positive fuchsin test. The reaction product was converted to its silver salt which was identical in its infrared spectrum with that of an authentic specimen.[20]

Lycorenine.—The alkaloid was obtained in trace amounts from *Lycoris radiata* Herb. by a conventional procedure[21] and recrystallized from methanol–acetone for analysis; m.p. 198–200°; $[\alpha]^{24}D$ +144° (*c* 1.03, methanol); $[\alpha]^{25}D$ +180° (*c* 1.12, chloroform). The material was identical with an authentic specimen kindly furnished by Prof. S. Uyeo.

Anal. Calcd. for $C_{18}H_{23}NO_4$: C, 68.12; H, 7.31; N, 4.41. Found: C, 68.21; H, 7.33; N, 4.34.

A solution of 94 mg. of lycorenine in 31 ml. of chloroform was oxidized by the above method with 0.5 g. of manganese dioxide. After 1.75 hours, the reaction mixture was filtered and the manganese dioxide was washed with ethanol. The combined organic solutions were concentrated to a brown oil that was triturated with ethyl acetate. Fractional crystallization from ethyl acetate gave 14 mg. of impure lycorenine, m.p. 182–188° and 30 mg. of a lactone, m.p. 174–176°, a portion of which was sublimed for analysis, m.p. 175–176°, $[\alpha]^{25}D$ +93.6° (*c* 0.84, chloroform). The compound showed strong lactone absorption in chloroform at 5.84 μ.

Anal. Calcd. for $C_{18}H_{21}NO_4$: C, 68.55; H, 6.71; N, 4.44. Found: C, 68.46; H, 6.61; N, 4.66.

---

[18] M. Freund and W. Will, *Ber.*, **20**, 2401 (1887).

[19] G. F. Woods, *Org. Syntheses*, **27**, 43 (1947).

[20] W. W. Westerfield, *J. Biol. Chem.*, **143**, 177 (1942).

[21] W. C. Wildman and C. J. Kaufman, THIS JOURNAL, **76**, 5815 (1954).

BETHESDA 14, MARYLAND

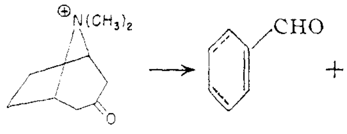
[CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY OF CORNELL UNIVERSITY AND MASSACHUSETTS INSTITUTE OF TECHNOLOGY]

Elimination Reactions of Bicyclic Quaternary Salts. I. The Base Degradation of Tropinone Methiodide[1]

BY J. MEINWALD, S. L. EMERMAN, N. C. YANG AND G. BÜCHI

RECEIVED JANUARY 26, 1955

The base degradation product of tropinone methiodide (I), hitherto considered to be a dihydrobenzaldehyde (II), is shown to be a mixture of cycloheptadienones. One component of the mixture, cycloheptadien-3,5-one (VI), has been isolated and characterized. Evidence for the formation of cycloheptadien-2,4-one (V) was also obtained. The Diels–Alder reactions of these dienones as well as of tropone and tropilidene are discussed.



+ $(CH_3)_2NH$ (1)

I II

The structure of tropinone is firmly established on the basis of sound degradative evidence supplemented by independent syntheses.[2] The report that tropinone methiodide (I) is converted under a variety of basic conditions into dimethylamine and a *dihydrobenzaldehyde* (II) according to equation 1 is, therefore, rather surprising.[3] Such a transformation would necessitate the contraction of the seven-membered ring to a cyclohexane derivative. Several different base-catalyzed ring contractions of carbonyl compounds are well known, which provide some formal analogy for the reported skeletal rearrangement of tropinone. One of these is the benzilic acid rearrangement of cyclic α-diketones,[4] a second is the Faworskii rearrangement of α-haloketones[5] and a third is the conversion of tropolone and its derivatives into benzenoid compounds.[6] It does not seem possible, however, to construct mechanisms directly related to any of the mechanisms of the above-mentioned rearrangements, which would be capable of accommodating the tropinone ring contraction. Since the formation of a dihydrobenzaldehyde seemed intrinsically unlikely, and since the structural evidence available

---

[1] A preliminary Communication of some of the results reported in this paper has appeared in *Chemistry and Industry*, 1063 (1953).

[2] For convenient reviews of the chemistry of tropinone see T. A. Henry, "The Plant Alkaloids," Churchill, Ltd., London, 1949, 4th Edn., or R. H. F. Manske and H. L. Holmes, "The Alkaloids," Academic Press, Inc., New York, N. Y., 1950, Vol. 1.

[3] (a) The fact that this transformation could be carried out under relatively gentle conditions was initially considered to provide evidence for the presence of a bridged cyclohexane nucleus in tropinone. When later developments disproved this hypothesis, the transformation seems to have been ignored or forgotten. The reaction was discovered almost simultaneously by R. Willstätter, *Ber.*, **29**, 393 (1896); and G. Ciamician and P. Silber, *ibid.*, **29**, 490 (1896). The second double bond in II was postulated to be in either of the two dotted positions. (b) The same "dihydrobenzaldehyde" had been obtained earlier from anhydroecgonine dibromide: see A. Einhorn, *ibid.*, **26**, 451 (1893); A. Eichengrün and A. Einhorn, *ibid.*, **23**, 2870 (1893).

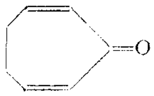
[4] Two examples of this type of contraction are cited by R. C. Fuson, "Advanced Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 1950, p. 360. For a discussion of the reaction mechanism see C. K. Ingold, "Structure and Mechanism in Organic Chemistry," Cornell University Press, Ithaca, N. Y., 1953, p. 480.

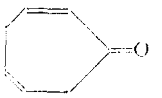
[5] R. B. Loftfield, THIS JOURNAL, **73**, 4707 (1951).

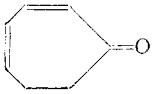
[6] See, for example, W. von E. Doering and L. H. Knox, *ibid.*, **74**, 5683 (1952).

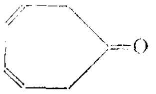
for the degradation product[3a,b] appeared equivocal, a reinvestigation of the nature of Willstätter's product has been undertaken.[7]

The degradation product to be expected would be simply cycloheptadien-2,6-one (III) or perhaps some double bond isomer (IV–VI). The aim of the initial experiments was, therefore, to distinguish between the cycloheptanone and cyclohexanone skeletons for this material.


III


IV


V


VI

Under a variety of basic reaction conditions, tropinone methiodide[8,9] gave rise to a product, C_7H_8O, in about 30% yield. This product, which had an odor strongly reminiscent of benzaldehyde, reduced Tollens reagent and Fehling solution, but failed to give a Schiff aldehyde test. It seems reasonable to assume that it is the same material that the earlier workers had in hand. The complexity of the infrared spectrum of this product (including five bands in the double bond stretching region) as well as the complexity of its ultraviolet spectrum (showing strong absorption at 214 and 291 mμ, the intensities of which varied from run to run) pointed to a mixture of absorbing species being present, rather than any single chemical individual. The crude mixture took up two moles of hydrogen over Adams catalyst, and gave rise to cycloheptanone, as was demonstrated by comparison with an authentic sample[10] *via* infrared spectra, melting points and mixture melting points of semicarbazones and 2,4-dinitrophenylhydrazones. *Skeletal rearrangement during the elimination reaction is thus precluded.*

It remains to identify the specific components in this mixture. One conclusion which can be drawn without any additional data is that cycloheptadien-2,4-one (V) must be present, since it alone could account for the ultraviolet absorption at 291 mμ.[11] The facts that the crude degradation product gave rise to a semicarbazone, m.p. 119–123°, $\lambda\lambda_{\max}$ 223 mμ (log ϵ 4.02) and 303 mμ (log ϵ 3.56),[12] and to a 2,4-dinitrophenylhydrazone, m.p. 144–147°, $\lambda_{\max}$ 388 mμ (log ϵ 4.46), are in accord with the presence of this isomer, but this evidence is weakened by the possibility of double bond migration during the formation of the derivatives. There is also a strong suggestion that cycloheptadien-3,5-one (VI) is contained in the mixture, since it is unique in possessing the unconjugated carbonyl group whose presence is indicated by the 5.85 μ band in the infrared.[13]

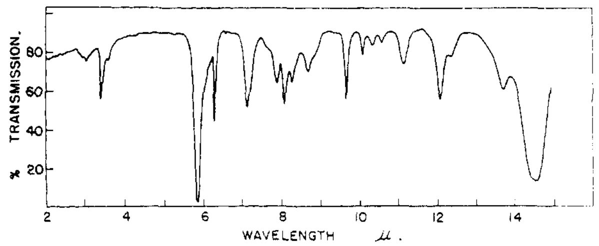


Fig. 1.—Infrared absorption spectrum of cycloheptadien-3,5-one.

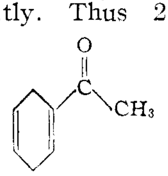
Pursuing the characterization of these dienones further, an attempt was made to isolate pure components by fractional distillation. The effort was rewarded by partial success; an initial fraction, b.p. 45° (4.9 mm.), consisted of nearly pure cycloheptadien-3,5-one (VI). The structural assignment rests on the following data:

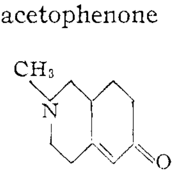
(1) The double bond region of its infrared spectrum showed only two maxima, 5.85 and 6.27 μ (see Fig. 1). The former provides direct evidence for an isolated carbonyl function.

(2) A semicarbazone of this fraction showed $\lambda_{\max}$ 223 mμ (log ϵ 4.17) typical of a saturated semicarbazone, and only weak absorption at longer wave lengths.

(3) A 2,4-dinitrophenylhydrazone showed $\lambda_{\max}$ 371 mμ (log ϵ 4.35) and no second maximum at longer wave lengths.

The ultraviolet spectrum of VI showed relatively weak absorption at 290 μ (log ϵ 2.75), but had a broad peak in the region of 213–214 mμ (log ϵ 3.74). This observation is surprising, since the absorption is not in accord with the spectrum of 1,3-cycloheptadiene ($\lambda_{\max}$ 248, log ϵ 3.87),[14] which might appear at first sight to be a suitable model compound. The most reasonable rationalization of this discrepancy is that there is some sort of transannular interaction between the diene system and the carbonyl group. Several cases of the displacement of *enone* absorption maxima by nearby but unconjugated groups have come to light recently. Thus 2,5-dihydroacetophenone (VII)


VII


VIII

---

[7] These studies were begun independently at the Massachusetts Institute of Technology and Cornell University, and were continued coöperatively. Those results not included in the preliminary communication (ref. 1) were obtained mainly in the latter laboratory.

[8] Tropinone was prepared *via* the now standard "biogenetic" route. The authors are indebted to Dr. Max Tishler of Merck and Co., as well as to Dr. Alex Nickon and Prof. L. F. Fieser of Harvard University, for generous gifts of tropinone during the early phases of the work.

[9] L. C. Keagle and W. H. Hartung, This Journal, **68**, 1608 (1946).

[10] Cycloheptanone was kindly supplied by Prof. A. T. Blomquist.

[11] E. E. van Tamelen and G. T. Hildahl, This Journal, **75**, 5451 (1953) have reported $\lambda_{\max}$ 292 mμ, ϵ 5400 for V. Eucarvone, with one extra substituent on the dienone system, shows $\lambda_{\max}$ 303 mμ, log ϵ 3.83, according to Y. R. Naves and P. Ardizio, *Helv. Chim. Acta*, **32**, 329 (1949).

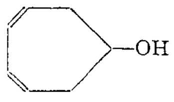
[12] *Cf.* Eucarvone semicarbazone $\lambda\lambda_{\max}$ 223.5 mμ (log ϵ 4.02) and 309 (log ϵ 4.21) reported by Naves and Ardizio, ref. 11.

[13] Although it is unlikely that either V or VI would be produced as initial products, the opportunity for isomerization during the degradation is obviously present. In experiments in which the base treatment was limited to only one minute, and the product worked up immediately, it was noted that no $\lambda_{\max}$ at 291 mμ appeared in the ultraviolet spectrum of the total crude product.

[14] E. Pesch and S. L. Friess, This Journal, **72**, 5756 (1950).

shows a bathochromic shift of *ca.* 10 mμ,[15] while the bicyclic structure VIII and its methiodide show hypsochromic shifts of 8 and 19 mμ, respectively.[16,17] Although these examples demonstrate that neighboring unsaturation or dipoles can influence enone absorption, there do not seem to be data recorded on which to base expectations concerning similar influences on *diene* absorption. At this stage, therefore, the ultraviolet spectrum of VI does not provide a structural clue, but rather poses a separate problem.

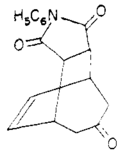
Confirmation of the conclusion that the first distillation fraction consists of VI was provided by the reduction of this compound to cycloheptadien-3,5-ol (IX) by sodium borohydride. The structure of this alcohol follows from its ultraviolet spectrum (λ_{max} 242–245 mμ, log ϵ 3.80), showing typical cycloheptadiene absorption. It is further supported by the failure of manganese dioxide to oxidize it to a ketone, a reaction which would be expected to occur readily for any of the other double bond isomers.[18]



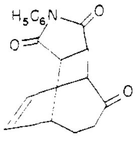
IX

Although VI could be isolated in reasonably pure state, higher boiling fractions were all mixtures enriched to varying degrees in V. Sodium borohydride reduction of these dienones gave rise to mixed dienols which were partially reconverted to V by manganese dioxide, as revealed by the reappearance of the 291 mμ maximum in the ultraviolet region.

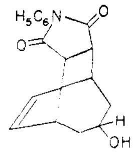
With a view to exploring the reactions of these dienones in greater detail, a series of Diels–Alder reactions was carried out. Cycloheptadien-3,5-one (VI) reacted slowly with N-phenylmaleimide to yield an adduct, $C_{17}H_{15}O_3N$, m.p. 201–204°. However, fractions of degradation product enriched in cycloheptadien-2,4-one (V) gave rise to the same adduct. In view of the expected interconvertibility of V and VI, it is impossible to predict whether this adduct should have structure X or XI.[19] Decision in favor of XI was made on the basis of two independent sets of experiments. The first of these consisted of an unambiguous synthesis of structure X *via* the dienol IX, in which there should be no double bond mobility. The dienol IX reacted with N-phenylmaleimide to give the adduct XII, m.p. 185–188°, which gave X, m.p. 188–191°, on Oppenauer oxidation. Direct comparison of infrared spectra of X with the adduct obtained from the dienones showed the two ketones to be different. This finding indicated that the dienone adduct must be XI. The structural problem was solved directly by a synthesis of XV from tropone (XIII)[20] *via* a Diels–Alder addition[21] followed by catalytic hydrogenation of the adduct (XIV). Catalytic hydrogenation of the dienone adduct, m.p. 201–204°, gave rise to a product indistinguishable from XV prepared from tropone. It may therefore be concluded that the dienone adduct has structure XI, derived from cycloheptadien-2,4-one.



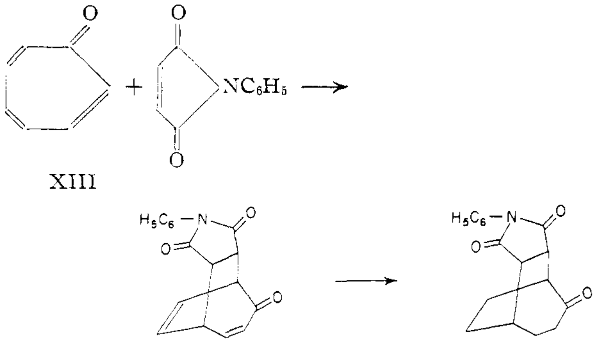
X



XI



XII

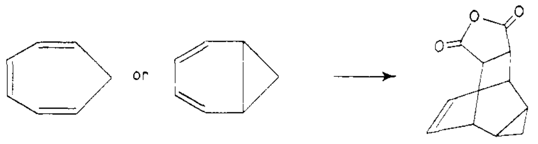


XIII

XIV

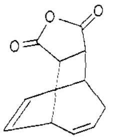
XV

It is interesting to note that at the same time the identity of the reduced dienone adduct with the reduced tropone adduct supports structure XI for the former, a perhaps more significant result of this correlation is its demonstration that tropone itself reacts normally with dienophiles. To assume tacitly that tropone would react as a typical diene might be unjustified in the light of its many unique properties and in view of the abnormal behavior of tropilidine (XVI) in the Diels–Alder



XVI

XVII



XVIII

---

(15) K. Bowden and E. R. H. Jones, *J. Chem. Soc.*, 52 (1946); E. A. Braude, E. R. H. Jones, F. Sondheimer and J. B. Toogood, *ibid.*, 607 (1949).

(16) V. Georgian, *Chemistry and Industry*, 930 (1954).

(17) A. Marchant and A. R. Pinder, *ibid.*, 1261 (1954).

(18) For recent examples of the use of this highly specific oxidant for allyl alcohols, see C. Amendolla, G. Rosenkranz and F. Sondheimer, *J. Chem. Soc.*, 1226 (1954); and M. Harfenist, A. Bavley and W. A. Lazier, *J. Org. Chem.*, **19**, 1608 (1954).

(19) (a) The stereochemistry shown here and henceforth is arbitrarily assumed on the basis of (1) maximum overlap of unsaturation in the transition state and (2) minimum steric repulsion in the final products. (b) In an exploratory experiment this ketone adduct was reduced with sodium borohydride and compared with authentic XII (described below). Although the two compounds were different, no conclusion can be drawn, due to the possibility of stereoisomerism at the carbon bearing the hydroxyl.

(20) Tropone was prepared by a bromination–dehydrobromination procedure, starting with mixed dienones (dihydrotropones). This series of reactions provides a direct path for the conversion of tropinone into tropone.

(21) The ability of tropone to participate in a Diels–Alder reaction with maleic anhydride has already been demonstrated (T. Nozoe, T. Mukai, K. Takase and T. Nagase, *Proc. Japan Acad.*, **28**, 477 (1952); *C. A.*, **48**, 2678 (1954)), although the structure of the adduct was not proven.

reaction. The tropilidene–maleic anhydride adduct has recently been shown to possess structure XVII, derived from norcaradiene, rather than structure XVIII.[22] Tropone, on the other hand, would not be expected to behave analogously, since such behavior would necessitate generating a cyclopropanone ring.

The study of the degradation reactions of some closely related bicyclic molecules is now in progress.

Experimental[23]

Tropinone Methiodide (I).—Small quantities of succinaldehyde dioxime were converted into tropinone by a modification of the Robinson "biosynthesis,"[9,24] using acetone dicarboxylic acid[25] and methylamine hydrochloride. Since difficulty was encountered in preparing the dioxime from pyrrole,[9,26] this starting material was abandoned in favor of 2,5-diethoxytetrahydrofuran.[27] Hydrolysis of this furan in aqueous hydrochloric acid, followed by neutralization with calcium carbonate, furnished aqueous solutions of succindialdehyde suitable for use in the subsequent condensation with acetone dicarboxylic acid and methylamine.[9] Treatment of the crude tropinone with methyl iodide gave the crystalline methiodide I.

Degradation of Tropinone Methiodide.—Tropinone methiodide (I) (35 g., 0.12 mole) and sodium bicarbonate (21 g., 0.25 mole) were dissolved in hot water and steam distilled for 30 minutes. (Treatment of I with silver oxide, followed by filtration and steam distillation, failed to give the 80% yield of degradation product reported by Willstätter.[3a]) The distillate contained oily yellow droplets, which were extracted into ether. After drying over magnesium sulfate, the ether extract was evaporated down to give 4.3 g. (32%)[28] of reddish liquid. This product, with a penetrating, benzaldehyde-like odor, reduced Tollens reagent and Fehling solution in the cold, but did not affect Schiff reagent.[29]

The infrared spectrum of crude product included strong bands at 5.85 and 6.03 μ, moderate bands at 6.13, 6.27 and 6.32 μ. In the ultraviolet: $\lambda_{\max}^{\mathrm{EtOH}}$ 291 mμ, log ε 3.26; at 210 mμ, log ε is 3.70. The product yielded a crude semicarbazone, m.p. 119–123°, $\lambda\lambda_{\max}$ 223 mμ (log ε 4.02) and 303 mμ (log ε 3.56).

The 2,4-dinitrophenylhydrazone decomposed on attempted recrystallization from ethanol. The crude derivative was chromatographed on silica gel, with benzene as the eluent. The initial fraction gave highest-melting solid, m.p. 144–147°, $\lambda\lambda_{\max}^{\mathrm{CHCl_3}}$ 265, 388 mμ; log $\epsilon_{\max}$ 4.11, 4.46. Attempts to prepare the oxime and phenylhydrazone[3b] from undistilled degradation product were unsuccessful.

Distillation of Degradation Product.—Careful distillation of the degradation product through a thirty inch Podbielniak partial reflux column afforded a colorless, constant-boiling first fraction (A) and increasingly yellowish fraction (B) which boiled over a considerable range.

Fraction A: b.p. 45.0° (5.0 mm.), $n^{20}\mathrm{D}$ 1.5130, $d^{20}{}_4$ 1.028, *MR*D calcd. (as VI) 31.53, found 31.57, infrared max. at 5.85 μ (strong) and 6.27 μ (moderate) (see Fig. 1), $\lambda_{\max}^{\mathrm{EtOH}}$ 213–214 mμ, log $\epsilon_{\max}$ 3.74. Fraction A yielded a semicarbazone, recrystallized from methanol with some decomposition, m.p. 135–140° $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 223, 300 mμ; log $\epsilon_{\max}$ 4.17, 2.71.

Anal. Calcd. for $C_8H_{11}ON_3$: C, 58.16; H, 6.71; N, 25.44. Found: C, 58.05; H, 6.55; N, 25.36.

An impure 2,4-dinitrophenylhydrazone from fraction A decomposed on attempted recrystallization, but could be eluted from a silica gel column with 30% ether in petroleum ether. The sharpest melting fraction showed m.p. 95–98°, $\lambda_{\max}^{\mathrm{CHCl_3}}$ 371 mμ, log $\epsilon_{\max}$ 4.35.

Anal. Calcd. for $C_{13}H_{12}O_4N_4$: C, 54.16; H, 4.20. Found: C, 54.50; H, 4.25.

Fraction B: b.p. 46–56° (5.0 mm.), $n^{20}\mathrm{D}$ 1.5209, infrared bands as in crude material, $\lambda_{\max}^{\mathrm{EtOH}}$ 291 mμ, log $\epsilon_{\max}$ 3.2 to 3.6 (in various runs).

Anal. Calcd. for C_7H_8O: C, 77.75; H, 7.45. Found (fraction B): C, 77.58; H, 7.26.

Rapid Degradation.—A 2-g. sample of I was degraded as described above, but the reaction mixture was steam distilled for only one minute. The usual work up procedure provided 0.1 g. of a liquid, infrared max. at 5.87, 6.08, 6.18 and 6.24 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 233 mμ, log $\epsilon_{\max}$ 3.80, with only weak absorption in the vicinity of 291 mμ.

Catalytic Hydrogenation of Degradation Product.—Platinum dioxide (0.1 g.) was suspended in a few ml. of ethyl acetate and prereduced in a standard semimicro hydrogenation apparatus. Undistilled degradation product (0.57 g., 0.0053 mole) was added. Absorption of hydrogen (0.0091 mole) stopped after 2.1 hours. Removal of catalyst by filtration and evaporation of the solvent at reduced pressure gave a tan liquid (0.58 g.). Infrared spectra of this liquid and a sample of authentic cycloheptanone,[10] repurified *via* its semicarbazone, were indistinguishable.

The hydrogenated product gave a semicarbazone, m.p. 163–164°, and a 2,4-dinitrophenylhydrazone, m.p. 146–147°, the melting points of which were undepressed by admixture with authentic samples of these derivatives. Infrared comparison of these materials with the authentic samples again revealed no differences.

Cycloheptadien-3,5-ol (IX).—A solution of sodium borohydride (1.2 g., 0.032 mole) in methanol (15 ml.) was added dropwise to VI (4.74 g., 0.040 mole) in methanol (10 ml.). The solution became copper colored after four hours standing. Dropwise addition of dilute sulfuric acid brought the *p*H to 7, discharged the color and gave a white precipitate. The mixture was filtered, added to a concentrated aqueous solution of ammonium sulfate contained in a separatory funnel, and extracted three times with ether. The combined ether extracts, after washing with water and drying over magnesium sulfate, were evaporated to give 3.90 g. (81%) of a pale yellow liquid. Vacuum distillation under nitrogen gave a colorless alcohol, b.p. 73.0° (25 mm.), $n^{20}\mathrm{D}$ 1.5265, infrared max. at 3.0 and 6.21 μ, $\lambda_{\max}^{\mathrm{EtOH}}$ 242–245 mμ, log $\epsilon_{\max}$ 3.84. The alcohol turned yellow on standing.

Anal. Calcd. for $C_7H_{10}O$: C, 76.32; H, 9.15. Found: C, 76.07; H, 9.12.

A *p*-nitrobenzoate, m.p. 81.5–82.5° after three recrystallizations from ethanol, was obtained in the standard fashion.

Anal. Calcd. for $C_{14}H_{13}O_4N$: C, 64.85; H, 5.05; N, 5.40. Found: C, 65.00; H, 5.12; N, 5.29.

Treatment of IX with Manganese Dioxide.—A sample of IX was stirred overnight in petroleum ether solution in the presence of a tenfold excess of active manganese dioxide.[30] The product, isolated by filtering the reagent and evaporating off the solvent, had an infrared spectrum identical with that of authentic IX.

Sodium Borohydride Reduction and Manganese Dioxide Reoxidation of Dienone Mixture.—Undistilled degradation product (0.34 g., $\lambda_{\max}^{\mathrm{EtOH}}$ 2.91 mμ, log $\epsilon_{\max}$ 3.38) was reduced with excess sodium borohydride, as described above. The product consisted of a brownish liquid (0.19 g.) with infrared

---

[22] K. Alder and G. Jacobs, *Ber.*, **86**, 1528 (1953). *Cf.* E. P. Kohler, M. Tishler, H. Potter and H. T. Tompson, This Journal, **61**, 1057 (1939); and W. von E. Doering and L. H. Knox, *ibid.*, **73**, 828 (1951).

[23] All melting points are uncorrected. Analyses are by Mr. M. Libowitz, Geller Labs., Hackensack, N. J., and Schwarzkopf Microanalytical Lab., Woodside, N. Y. Infrared spectra were recorded on a Perkin–Elmer double-beam spectrophotometer, Model 21; solids were determined as Nujol mulls. Ultraviolet absorption spectra were measured with a Beckman quartz spectrophotometer, Model DU.

[24] C. Schöpf and G. Lehmann, *Ann.*, **518**, 1 (1935).

[25] R. Adams, H. M. Chiles and C. F. Rassweiler, "Organic Syntheses," Coll. Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1947, p. 10.

[26] R. Willstätter and W. Huebner, *Ber.*, **40**, 3869 (1907).

[27] We are indebted to the Carbide and Carbon Chemicals Company for a very generous sample of this furan.

[28] This was the average yield of many runs.

[29] Willstätter, ref. 3a, reported that the crude material reddened Schiff reagent, reduced Fehling solution at elevated temperature, and reduced Tollens reagent in the cold. Probably the only significant conclusion to be drawn from these color tests is that the degradation product is easily oxidized.

[30] This reagent was prepared by the procedure of J. Attenburrow, A. F. B. Cameron, J. H. Chapman, R. M. Evans, B. A. Hems, A. B. A. Jansen and T. Walker, *J. Chem. Soc.*, 1094 (1952).

bands at 5.85, 6.03, 6.13 and 6.32 μ greatly reduced in intensity compared to the starting material. The band at 6.27 μ was absent, the new bands at 3.0 and 6.21 μ appeared. In the ultraviolet region, this mixture showed $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 244, 292 mμ, $\log \epsilon_{\max}$ 3.74, 2.88. Thus the product appears to contain some of the cycloheptadien-3,5-one and cycloheptadien-2,4-one, as well as the corresponding alcohols.

The liquid mixture (58 mg.) was dissolved in a few ml. of petroleum ether and stirred for one hour in the presence of active manganese dioxide (600 mg.). The product was isolated as a pale yellow oil (35 mg.), and showed bands at 6.03, 6.13 and 6.32 μ, characteristic of the dienone V, as well as shoulders at 5.85 and 6.21 μ. In the ultraviolet, there were $\lambda\lambda_{\max}^{\mathrm{EtOH}}$ 241, 292 mμ, $\log \epsilon_{\max}$ 3.66, 3.34. The latter provides a good indication of the regeneration of V.

Diels–Alder Reaction of VI.—A distilled sample of VI (0.69 g.) was dissolved in dry benzene (25 ml.) and pure N-phenylmaleimide (1.01 g.) was added. The mixture was protected by a calcium chloride tube and refluxed under nitrogen for ten days. On the third day, the appearance of white crystals was noted. These increased perceptibly in quantity through the eighth day. On cooling, filtering and drying, 1.23 g. (76%) of well-formed crystals (XI) was obtained, m.p. 200–206°. Three crystallizations from benzene provided an analytical sample, m.p. 199–202°.

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.37; N, 4.98. Found: C, 72.83; H, 5.48; N, 5.05.

Diels–Alder Reaction of Dienone Mixture.—In a second experiment, a distillation cut which was chiefly V was used. A solution of ketone (2.20 g.) and N-phenylmaleimide (3.53 g.) in benzene (75 ml.) was refluxed for eight days. Crystals appeared within the first day. An adduct was isolated from this mixture which consisted of 3.40 g. (60%), m.p. 201–204° after two crystallizations from benzene. This adduct was shown to be XI by mixture melting point and infrared comparison.

Diels–Alder Reaction of Cycloheptadien-3,5-ol.—Distilled dienol (1.50 g.) was refluxed with N-phenylmaleimide (2.46 g.) in benzene (50 ml.) for seven days, as described above. No crystals appeared, but on cooling, 1.29 g. (33%) of star-shaped crystal masses (XII), m.p. 176–179°, separated. Two recrystallizations from benzene raised the melting point to 185–188°, which was unchanged by further recrystallization.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.29; H, 6.10; N, 4.89.

Reduction of XI by Sodium Borohydride.—A solution of the ketone adduct XI (1.85 g.) in chloroform and methanol was reduced with sodium borohydride (0.15 g.) in methanol in the usual way. Working up after five hours of reaction time yielded 1.54 g. of white crystals and a viscous liquid. Three crystallizations from benzene gave a product, m.p. 164–168° (forming an opaque melt which became clear at 172°). The infrared spectrum of this product differed markedly from that of XII.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.99; H, 6.20; N, 4.64.

Oppenauer Oxidation of XII.—Following the model procedure described in "Organic Reactions,"[31] the alcohol adduct XII (0.27 g.) underwent Oppenauer oxidation in the presence of toluene, cyclohexanone and freshly distilled aluminum isopropoxide. The usual isolation procedure yielded a white solid which on twofold recrystallization from benzene gave 0.15 g. (56%) of X, m.p. 188–191°. The product gave a positive test with hydroxylamine reagent, and had lost the hydroxyl band clearly visible in the infrared spectrum of the starting material. The infrared spectrum also differed markedly from that of the ketone adduct XI.

Anal. Calcd. for $C_{17}H_{15}O_3N$: C, 72.58; H, 5.37; N, 4.98. Found: C, 73.35; H, 5.63; N, 4.68.

Tropone (XIII).—A solution of undistilled degradation product (3.0 g., 0.028 mole) in 50 ml. of carbon tetrachloride was cooled to −5°. Bromine in carbon tetrachloride (71 ml. of 0.408 *M* solution, 0.028 mole) was slowly added, with stirring, producing a yellow solid. Removal of solvent at diminished pressure left a rapidly decomposing solid. Most of this residue dissolved, with evolution of gas, in water containing excess sodium carbonate (10 g.). The aqueous solution was extracted with five portions of ether. After drying over magnesium sulfate, the ether was evaporated to give 2.8 g. of a dark liquid. Distillation in an ordinary sidearm flask gave 0.7 g. of a tan liquid (XIII), b.p. 60–70° (0.1 mm.), $\lambda\lambda_{\max}^{H_2O}$ 224, 228, 231.5, 239, 312 mμ, $\log \epsilon_{\max}$ 4.30, 4.32, 4.33, 3.69, 3.92 (*cf.* Dauben and Ringold,[32] $\lambda\lambda_{\max}^{H_2O}$ 225, 228, 231.5, 239, 312.5 mμ, $\log \epsilon_{\max}$ 4.26, 4.34, 4.34, 4.10, 3.92).

The 2,4-dinitrophenylhydrazone,[21] thrice recrystallized from ethyl acetate–ethanol solutions, formed fine, purplish needles, m.p. 174–176°.

A sample of the original solid product was sublimed twice *in vacuo;* the ultraviolet spectrum in water containing a little sodium carbonate was that of relatively pure tropone, $\lambda\lambda_{\max}^{H_2O}$ 225, 228, 232, 239, 312, $\log \epsilon_{\max}$ 4.43, 4.36, 4.36, 4.12, 3.93. Calculation of extinction coefficients was based on the assumption that the solid was tropone hydrobromide, C_7H_7OBr.[33] This was confirmed by titration of an aqueous solution for bromide ion with silver nitrate, using eosin as an indicator (molecular weight calcd., 187; found, 196, 197).

Tropone Adduct (XIV).—A solution of distilled tropone (0.40 g.) and N-phenylmaleimide (0.70 g.) in xylene (15 ml.) was kept at 100–110° for two hours. Considerable amounts of solid crystallized out, as the solution became increasingly dark. On cooling, filtering and drying, 0.83 g. of grey crystals (XIV) was obtained. Two recrystallizations from benzene–chloroform and one from ethyl acetate–chloroform provided an analytical sample, m.p. 234–236°.

Anal. Calcd. for $C_{17}H_{13}O_3N$: C, 73.11; H, 4.69; N, 5.02. Found: C, 73.11; H, 4.41; N, 5.29.

Hydrogenation of Diels–Alder Adducts XI and XIV. A.—A suspension of platinum dioxide (80 mg.) in ethyl acetate was prereduced and the tropone adduct XIV (186 mg.) was added. Hydrogenation became very slow and was stopped after the uptake of 43.6 ml. (at 20° and 733 mm.). The product was isolated and recrystallized from ethyl acetate to give 90 mg. of white needles (XV), m.p. 169–174°. Another run yielded a product, m.p. 168–170°.

B.—The ketone adduct XI (228 mg.) was hydrogenated as described above. Hydrogenation proceeded slowly beyond the theoretical extent of 20.0 ml. (at 19° and 740 mm.), and was stopped after the uptake of 32.4 ml. Isolation of the product and recrystallization from benzene gave 190 mg. of white needles (XV) m.p. 165–170° (m.p. 171–174° in another run). The mixture melting point of these needles with the product obtained in part A above showed no depression (m.p. 168–172°). Infrared spectra of both samples were indistinguishable. Hydrogenated adduct recovered from the mother liquors of both crystallizations yielded an analytical sample, m.p. 170–173°.

Anal. Calcd. for $C_{17}H_{17}O_3N$: C, 72.06; H, 6.05; N, 4.94. Found: C, 72.02; H, 5.82; N, 4.76.

ITHACA, N. Y.

---

[31] C. Djerassi, "Organic Reactions," Vol. VI, John Wiley and Sons, Inc., New York, N. Y., 1951, p. 235.

[32] H. J. Dauben and H. J. Ringold, THIS JOURNAL, **73**, 876 (1951).

[33] W. von E. Doering and F. L. Detert, *ibid.*, **73**, 876 (1951).