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The Synthesis of Substituted Tricyclo[6.2.2.0^{2,7}]dodecanes from 2-Cyclohexenone[1]

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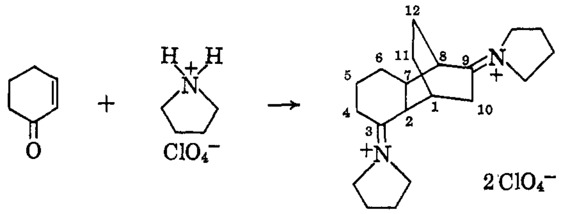
The reaction between 2-cyclohexenone and pyrrolidine perchlorate has been shown to yield di-N,N′-tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate (**1**). The basic skeletal structure was demonstrated by hydrolysis to tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (**10**) and Wolff–Kishner reduction to tricyclo[6.2.2.0^{2,7}]dodecane (**11**), which was prepared independently by catalytic reduction of the Diels–Alder dimer of 1,3-cyclohexadiene. The saturated hydrocarbon obtained from both routes was found to consist predominantly of the *cis* isomer of **11**, with a small amount of *trans* isomer present.

Condensation and alkylation reactions involving 2-cyclohexenones afford a considerable variety of products as a consequence of the number of reaction sites available on the α,β-unsaturated ketone and its related anion. Nearly every mode of condensation exhibited by these α,β-unsaturated ketones is also present in the various self-condensation reactions of 2-cyclohexenones.[4-8] We can now add an effective over-all dimerization reaction of 2-cyclohexenone which has its basis in enamine[9-11] and iminium salt[12,13] chemistry. In seeking to extend the direct condensation reaction of aldehydes and ketones with secondary amine perchlorates[12] to α,β-unsaturated ketones, we have found that the product of reaction of 2-cyclohexenone with pyrrolidine perchlorate in refluxing benzene is not the result of simple 1:1 condensation, N-(2-cyclohexenylidene)pyrrolidinium perchlorate, but possesses a dimeric structure, that of di-N,N′-tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate (**1**).



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Although the conversion of enones to dienamines has been well documented[14-16] and numerous reactions of the dienamines have been studied,[9,14-29] we find no previous account of the "dimerization" of 2-cyclohexenone through its enamine or iminium salt. When equimolar portions of 2-cyclohexenone and pyrrolidine perchlorate, plus 1 drop of pyrrolidine, were heated at reflux, azeotropic distillation afforded the theoretical amount of water within 4 hr. The purification of the crude product obtained included chromatography of a nitromethane solution on alumina, solution precipitation from a mixed solvent of nitromethane, ethanol, and ether, and final recrystallization from acetonitrile. The empirical formula of the major

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(2) Sinclair Refining Co. Fellow in Organic Chemistry, 1962–1963.

(3) Hoffmann-La Roche, Inc., Fellow in Chemistry, 1963–1964.

(4) W. I. Taylor, *Chem. Ind.* (London), 252 (1954).

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(19) G. Opitz and W. Merz, *Ann.*, **652**, 139 (1962).

(20) J. C. Babcock and R. L. Pederson, U. S. Patent 2,990,400 (June 27, 1961); *Chem. Abstr.*, **55**, 23604 (1961).

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(22) R. B. Millward, *J. Chem. Soc.*, 26 (1960).

(23) S. Hünig, E. Benzing, and K. Hübner, *Ber.*, **94**, 486 (1961).

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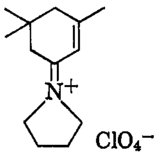
product corresponded to $C_{10}H_{16}ClNO_4$, but the presence in the infrared spectrum of two absorption bands at 1640 and 1678 cm^{-1}, indicative of two different $C{=}N^+$ groups, pointed to molecular formula $C_{20}H_{32}Cl_2N_2O_8$. The absence of conjugation was shown by the lack of absorption in the ultraviolet spectrum[30] of an acetonitrile solution, and the absence of any olefinic protons was shown by the nmr spectrum of a trifluoroacetic acid solution. Previously reported spectroscopic data[16,19,31,32] and those for the model eniminium salt, N-(3,5,5-trimethyl-2-cyclohexenylidene)pyrrolidinium perchlorate (**2**), obtained by treatment with perchloric acid of the enamine of isophorone, 1-N-pyrrolidyl-3,5,5-trimethyl-1,3-cyclohexadiene, namely, $\nu_{max}^{CHCl_3}$ 1610 cm^{-1}, $\lambda_{max}^{CH_3CN}$ 268 mμ (ϵ 19,800), nmr τ value (CF_3COOH) at 3.49 (=C—H), would have ensured detection of a conjugated function in the C_{20} product from 2-cyclohexenone. The absence of a carbon–carbon double bond directed us to a tricyclic structure. The assumption of a plausible mechanistic sequence involving nucleophilic addition of enamine to a conjugated system, twice repeated, and one which neglected the possibility of small- or medium-ring formation[6] led us to favor the formulation **1** (see Scheme I). If N-(2-cyclohexenylidene)pyrrolidinium perchlorate (**3**, ClO_4^-) is considered to be formed initially and if all the bases and conjugate acids are considered to be in equilibrium, the reaction of **3** with N-(1,3-cyclohexadienyl)pyrrolidine (**4**), culminating in **1** (path A), may be seen to involve two Michael additions and well-recognized enamine equilibria. Consideration of a parallel sequence (path B) based on the reaction of 2-cyclohexenone with its dienamine **4** and leading to the bisenamine **5** corresponding to **1** encouraged us to carry out the 2-cyclohexenone–pyrrolidine condensation in the absence of acid catalyst, with the positive results which will be described in due course.



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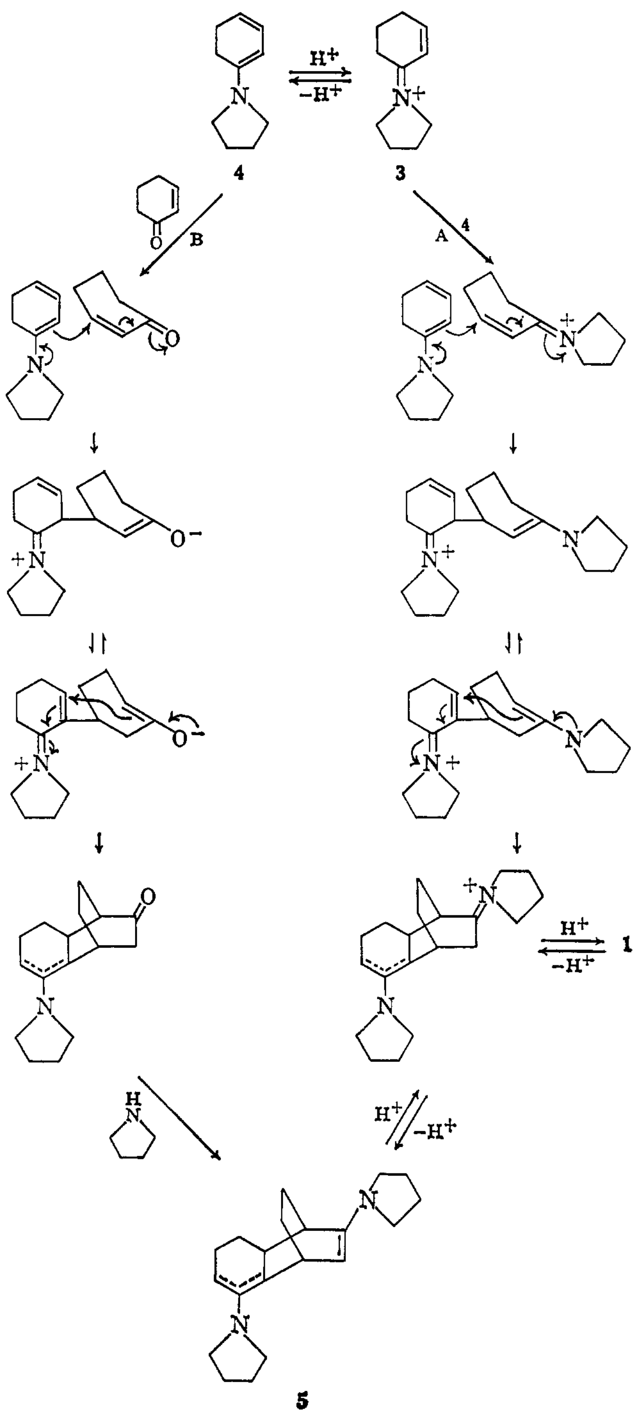
Let us first focus attention on the procedures which were used to assign structure **1** to the C_{20} product from 2-cyclohexenone and pyrrolidinium perchlorate and to exclude other possibilities. This compound could be reduced, either with hydrogen and platinum or with sodium borohydride in 2-propanol, to a compound having four more hydrogen atoms, for which the nmr spectrum gave evidence of the absence of residual unsaturation and the infrared spectrum indicated, by the loss of absorption between 1600 and 1700 cm^{-1} and the appearance of new absorption at 3190 cm^{-1}, that the conversion $>C{=}\overset{+}{N}<\ \rightarrow\ >CH{-}\overset{+}{N}H<$ had taken place. In anticipation of further results which will be described, structure **6**, di-N,N′-tricyclo[6.2.2.$0^{2,7}$]dodeca-3,9-diylpyrrolidine, may be assigned to the reaction product. For comparison, N-cyclohexylidenepyrrolidinium perchlorate is reduced by sodium borohydride[33] to the corresponding saturated amine salt, N-cyclohexylpyrrolidine perchlorate, whereas a conjugated eniminium salt such as N-(3,5,5-trimethyl-2-cyclohexenylidene)pyrrolidinium perchlorate (**2**) is reduced to the corresponding β,γ-unsaturated amine salt, N-(3,5,5-trimethyl-2-cyclohexenyl)pyrrolidine perchlorate, with readily recognizable functionality: $\nu_{max}^{CHCl_3}$ 1667 (C=C), 3070 (N^+—H) cm^{-1}; nmr τ value 4.55 (=C—H). When the crude bisiminium salt **1** was treated with boiling water, a partially hydrolyzed product was isolated which possessed a ketone carbonyl (ν_{max}^{Nujol} 1703 cm^{-1}),

SCHEME I



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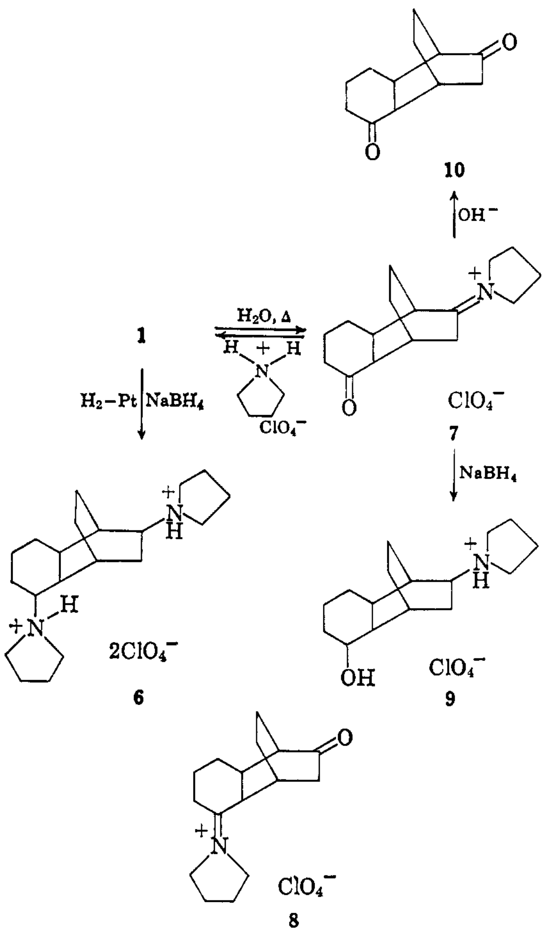
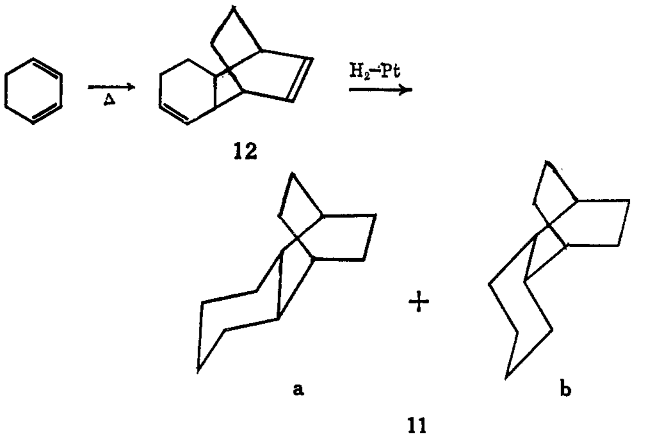
a $C{=}N^+$ group (1675 cm^{-1}), and no $N^+{-}H$. Based on the working hypothesis of structure **1** this compound would be formulated as **7**, N-tricyclo[6.2.2.$0^{2,7}$]dodec-3-on-9-ylidenepyrrolidinium perchlorate, owing to the carbonyl stretching frequency, which is in the normal range for substituted cyclohexanones, rather than to the alternate **8**, which would be expected to exhibit a carbonyl stretching frequency in the infrared close to that (1731 cm^{-1}) observed for bicyclo[2.2.2]octanone.[34] When the ketoiminium salt was treated with pyrrolidine perchlorate in refluxing benzene the bisiminium salt was regenerated, showing that no skeletal rearrangement had taken place during the hydrolysis. It could be reduced with sodium borohydride to a product having four additional hydrogens, showing infrared maxima for O—H (3530 cm^{-1}) and $N^+{-}H$ (3030 cm^{-1}), and therefore formulated as N-tricyclo[6.2.2.$0^{2,7}$]dodec-3-ol-9-ylpyrrolidine perchlorate (**9**). Basic hydrolysis of either ketoiminium salt **7** or bisiminium salt **1** yielded a tricyclic diketone with the formula, $C_{12}H_{16}O_2$, confirmed by molecular weight determination. The infrared spectrum showed one carbonyl vibration at 1706 cm^{-1}, in the range for substituted cyclohexanones, and another at 1727 cm^{-1}, indicative of the carbonyl on a bridging ethano group.[34] It was at this stage that the structures throughout the series became secure, since it was possible to establish in this diketone the tricyclo[6.2.2.$0^{2,7}$]dodecane ring system and the location of the two carbonyl groups at positions 3 and 9, *i.e.*, the tricyclo[6.2.2.$0^{2,7}$]dodecane-3,9-dione structure (**10**). Treatment of the diketone with pyrrolidine perchlorate yielded a mixture of ketoiminium salt **7** and bisiminium salt **1**, again indicative of the absence of gross skeletal rearrangement in the chemical interrelation of members of this series. (See Scheme II.)

SCHEME II



The number of methylenes α to carbonyl was determined by the formation of a dipiperonylidene derivative, as indicated by elemental analysis and by the nmr spectrum, which showed a ratio of the total of benzylidene, methylenedioxy, plus aromatic protons to the rest of the hydrogens of 1:1.06. The expected ratio is 1:1. This diketone derivative had a strong broad infrared maximum at 1682 cm^{-1} and an ultraviolet maximum in ethanol at 331 mμ (log ε 4.56). Comparison with the spectral properties of 2,6-dipiperonylidenecyclohexanone, ν_{max}^{Nujol} 1658 cm^{-1}, λ_{max}^{EtOH} 370 mμ (log ε 4.37), showed clearly that the two piperonylidene groups in the diketone derivative could not be α,α' to only one of the carbonyl groups, but that each was associated with one carbonyl. Had there been three methylene groups adjacent to the two carbonyls, as in the case of tricyclo[6.2.2.$0^{2,7}$]dodecane-4,10-dione,[3] a tripiperonylidene derivative would have been produced under the same conditions. Treatment of the diketone with deuterium oxide in the presence of base led to the incorporation of 4.85 ± 0.25 atoms of deuterium/molecule. This indication of a total approaching five replaceable hydrogens α to the two carbonyl groups offered corroboration for the position of the carbonyl groups as indicated in **10**. The ring system of tricyclo[6.2.2.$0^{2,7}$]dodecane-3,9-dione was established by Wolff–Kishner reduction of the bissemicarbazone to tricyclo[6.2.2.$0^{2,7}$]dodecane (**11**). The structure proof of this hydrocarbon rests upon spectral comparison with an authentic sample obtained by reduction of the Diels–Alder dimer **12** of cyclohexadiene.[8,35,36] While the infrared spectra of **11** obtained from both routes were essentially identical, the nmr spectra of the two samples exhibited minor differences. These spectral discrepancies prompted an investigation of the purity of hydrocarbon **11**.



The establishment of the stereochemistry at the ring junction (C-2 and C-7) in the series of compounds investigated (**1**, **5**, **6**, **7**, **9**, **10**) has not been sought since equilibration of *cis* and *trans* isomers can occur

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[34] R. Zbinden and H. K. Hall, Jr., *J. Am. Chem. Soc.*, **82**, 1215 (1960).

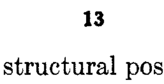
[35] K. Alder and G. Stein, *Ann.*, **496**, 197 (1932).

[36] B. A. Kazanskii and P. I. Svirskaya, *Zh. Obshch. Khim.*, **29**, 2588 (1959).

at virtually every stage from 2-cyclohexenone to products, owing to the presence of base in most of the reactions. Indeed, in considering the final Wolff–Kishner reduction which confirmed the tricyclic ring system, it was anticipated that this reduction of **10** would probably produce a mixture of *trans*- and *cis*-tricyclo[6.2.2.0^{2,7}]dodecane (**11a** and **b**). Using a gas-liquid partition chromatography column of tri-*o*-cresyl phosphate on firebrick, a packing which had been used[37] to separate *cis*- and *trans*-hydrindan and the isomeric bicyclo[5.2.0]nonanes, the Wolff–Kishner reduction product **11** was chromatographed. Two components were found to be present, the minor component of shorter retention time being present in amounts varying between 10 and 24% from one Wolff–Kishner reaction to another. When hydrocarbon **11**, obtained by the Diels–Alder route, was subjected to similar chromatography, the identical two components were found to be present, though the minor peak was present in smaller amount. Upon consideration of the methods of synthesis of the two samples of **11** in conjunction with an absence of any indication of nonisomeric contaminants (for example, a sample of **11** containing 24% of the minor component still had the correct analysis for pure hydrocarbon and had an infrared spectrum virtually identical with a sample containing but 6% of the contaminant), it was felt that the material present in minor amount was probably *trans*-tricyclo[6.2.2.0^{2,7}]dodecane while the major component was the *cis* isomer, as expected from a Diels–Alder reaction. Presumably, isomerization of diene **12** during hydrogenation over platinum is responsible for the small amount of *trans* isomer present in the fully reduced Diels–Alder product. It can also be noted that the relative retention times of the *cis* and *trans* isomers (*trans* off the column first), were like those found for the two bicyclic hydrocarbons previously separated on a similar column.[37]

Preparative gas–liquid partition chromatography enabled us to obtain both *cis* and *trans* isomers with better than 95% purity. It does not appear easy to correlate the minor infrared spectral differences between the isomers with corresponding differences in the spectra of *cis*- and *trans*-decalin[38] (in particular, the tertiary carbon–hydrogen stretching frequencies near 2860 cm^{-1} and the secondary carbon–hydrogen deformation frequencies near 1460 cm^{-1}). The nmr spectra, however, are considerably more informative. The main feature of the spectrum of the *cis* and predominant isomer is a strong, fairly sharp resonance at τ 8.46. The remainder of the spectrum consists of broad multiplets between τ 8.52 and 8.81, and at 8.94. In contrast, the nmr spectrum of the *trans* isomer lacks the sharp resonance at τ 8.46 and consists instead of several broad multiplets at τ 7.86–8.14, 8.25–8.55, 8.60–8.88, and 8.92–9.08. A broadened, more complex *trans* spectrum and relatively sharp *cis* spectrum have been found for the *trans*- and *cis*-decalins and hydrindans.[39,40] The *trans* configuration of tricyclo[6.2.2.0^{2,7}]dodecane (**11a**) is rigid, and consequently the axial and equatorial protons will exhibit different chemical shifts and more complex coupling patterns, with resulting broadened signals. The *cis* configuration of tricyclo[6.2.2.0^{2,7}]dodecane (**11b**) is flexible, and two chair conformations of the cyclohexane moiety are interchangeable at a rate sufficient for the axial and equatorial protons to give averaged chemical shifts, affording narrow signals. In summation, the hydrocarbon obtained by Wolff–Kishner reduction of the bissemicarbazone (above) is a mixture of *cis*- and *trans*-tricyclo[6.2.2.0^{2,7}]dodecane, *cis* isomer predominating. With the ring system established and the carbonyl groups positioned at 3 and 9 (**10**), the rest of the compounds in the series have the structures shown (**1, 5, 6, 7, 9, 10**).

The postulated reaction path (A) leading to di-N,N′-tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate (**1**) from equimolar amounts of 2-cyclohexenone and pyrrolidine perchlorate suggested to us that normal synthesis conditions for enamines,[9] in this case 2-cyclohexenone, pyrrolidine, and a small amount of *p*-toluenesulfonic acid in refluxing benzene, could lead to the bisenamine **5**, probably mainly the isomer with the double bond at C-3, along the same reaction path. When these conditions were applied, the initial product could not be vacuum distilled conveniently owing to extensive decomposition and polymerization, but the presence of the enamine **5** in the crude reaction product was indicated by hydrolysis with dilute sodium hydroxide[16] to afford about 51% over-all of tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (**10**), judged by nmr and infrared spectral comparison. The tricyclic diketone **10** was also one of the products obtained by a similar procedure, probably *via* reaction path B, from 2-cyclohexenone and pyrrolidine in the absence of acid catalyst,[9] judged by the same criteria. The diketone was not obtained when 2-cyclohexenone and triethylamine were refluxed in benzene, suggesting that pyrrolidine was not acting as a general base catalyst in the self-condensation of 2-cyclohexenone, but that it played a specific role.[41] That the diketone **10** did not result simply under the influence of the sodium hydroxide used for the hydrolysis[42] was indicated by the formation of a different major product when 2-cyclohexenone was stirred at 25° in 10% aqueous sodium hydroxide for 12 hr. The predominant product from this combination has been assigned structure **13**, 2-(3′-oxocyclohexyl)cyclohex-2-enone, on the basis of analysis and spectral evidence: $\nu_{max}^{CHCl_3}$ 1706 (C=O), 1668 (conjugated C=O), 1640 (C=C) cm^{-1}; λ_{max}^{EtOH} 233 mμ (ϵ 8000), 285 mμ (ϵ 112); nmr signal at τ 3.29 (triplet, 1H, J = 3.5 cps) indicative of one olefinic proton.



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While our initial structural postulate, which omitted from consideration the presence of a four-membered ring in the major product resulting from condensation

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[37] N. L. Allinger, M. Nakazaki, and V. Zalkow, *J. Am. Chem. Soc.*, **81**, 4074 (1959).

[38] J. Seidman, *Anal. Chem.*, **23**, 559 (1951).

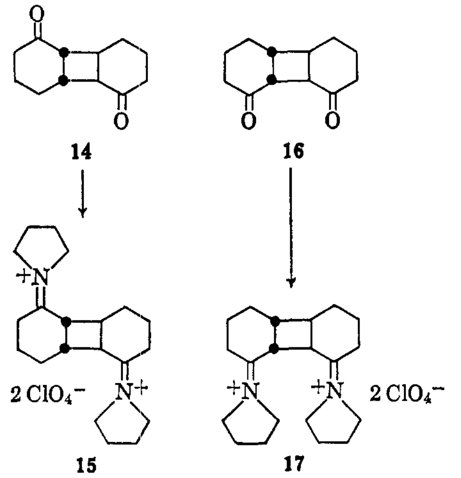
[39] J. A. Pople, W. G. Schneider, and H. J. Bernstein, "High Resolution Nuclear Magnetic Resonance," McGraw-Hill Book Co., Inc., New York, N. Y., 1959, p 399.

[40] W. B. Moniz and J. A. Dixon, *J. Am. Chem. Soc.*, **83**, 1671 (1961).

[41] *Cf.* F. H. Westheimer and H. Cohen, *ibid.*, **60**, 90 (1938).

[42] The collection of water during the heating of the benzene solution of 2-cyclohexenone and pyrrolidine indicated that prior condensation had actually occurred.

of 2-cyclohexenone with pyrrolidine perchlorate, has been shown to be correct, the reaction of certain electrophilic olefins with enamines may lead to cyclobutane derivatives.[10,43,44] Furthermore, since photodimers of 2-cyclohexenone containing a cyclobutane ring have recently been made available through the work of Eaton,[45–48] it became of interest for comparison purposes to convert these to the bisiminium salts isomeric with **1**. *cis,trans,cis*-Tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (**14**), mp 54.5–55.5°, was converted to di-N,N′-*cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate (**15**), mp 290–291° dec, $\nu_{\max}^{\text{Nujol}}$ 1650 cm^{-1}, with pyrrolidine perchlorate in refluxing benzene; *cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]-dodeca-3,12-dione (**16**), mp 79–80°, was converted to di-N,N′-*cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]dodeca-3,12-diylidenepyrrolidinium diperchlorate (**17**), mp 276–277° dec, $\nu_{\max}^{\text{Nujol}}$ 1647 cm^{-1}. Both were obviously different from **1** by spectral comparisons. Di-N,N′-*cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]deca-3,8-diylidenepyrrolidinium diperchlorate, mp >315° (*explodes*), $\nu_{\max}^{\text{Nujol}}$ 1710 cm^{-1}, was made in the same manner from *cis,trans,cis*-tricyclo[5.3.0.0^{2,6}]decane-3,8-dione, mp 125–126°, the photodimer of cyclopentenone.[46]



Experimental Section[49]

Di-N,N′-Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium Diperchlorate (1).—In 600 ml of benzene were placed 13 g (76 mmoles) of pyrrolidine perchlorate, 7.3 g (76 mmoles) of 2-cyclohexenone, and 1 drop of pyrrolidine. The mixture was heated with stirring at reflux for 4 hr under a Dean-Stark trap. The benzene was decanted and the semisolid orange-brown residue was washed with hot ethanol, followed by an ether wash, to afford 18.8 g (99%) of crude reddish product. After chromatography on 170 g of alumina with nitromethane, the material was dissolved in 30–50 ml of nitromethane, treated with 300 ml of methanol (or ethanol) and 600 ml of ether, and then cooled. The solid was collected, and the treatment was repeated twice more to yield 12 g (64%) of fairly pure brownish pink product. Further purification in this manner (with a proportional reduction in yield) afforded pure colorless product: mp 277–278° dec; $\nu_{\max}^{\text{KBr or Nujol}}$ 1640, 1678 cm^{-1} (C═N$^+$); nmr τ values (br, TFA–TMS), 5.89, 6.64, 7.08, 7.66, 8.00. The partially pure material could also be further purified by recrystallization from a saturated acetonitrile solution as colorless prisms, mp 285–287° dec (sintering at 283°).

Anal. Calcd for $C_{20}H_{32}Cl_2N_2O_8$: C, 48.10; H, 6.46; N, 5.61. Found: C, 47.93; H, 6.63; N, 5.41.

Di-N,N′-Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylpyrrolidine Diperchlorate (6). From Catalytic Hydrogenation.—A mixture of 0.605 g (1.2 mmoles) of di-N,N′-tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate and 0.06 g of platinum oxide in 200 ml of warm methanol was hydrogenated at atmospheric pressure and room temperature until hydrogen uptake ceased (2 hr). The catalyst was removed by filtration, and the solvent was removed *in vacuo*. The residue was recrystallized from nitromethane–ether to afford 0.452 g (75%) of crude, colorless product, mp 266–268° dec (further recrystallization raised the melting point to 272–274° dec), $\nu_{\max}^{\text{Nujol}}$ 3190 cm^{-1} (N$^+$-H).

Anal. Calcd for $C_{20}H_{36}Cl_2N_2O_8$: C, 47.71; H, 7.21; N, 5.57. Found: C, 47.43; H, 7.15; N, 5.45.

From Sodium Borohydride Reduction.—A solution of 0.085 g (0.17 mmole) of di-N,N′-tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate and 0.06 g (1.57 mmoles) of sodium borohydride in 120 ml of 2-propanol was heated under reflux with stirring for 17 hr. The solvent was removed *in vacuo*, and the remaining solid was dissolved in aqueous sodium hydroxide. The solution was extracted with ether, and the ether solution was dried over magnesium sulfate. The solution was acidified with 1:1 ethanol–perchloric acid to yield 0.069 g (81%) of colorless product, which after recrystallization from nitromethane–ether had mp 275.5–276° dec (undepressed by admixture with the product obtained by catalytic reduction); $\nu_{\max}^{\text{Nujol}}$ 3190 cm^{-1} (N$^+$–H); nmr τ values (TFA–TMS), 6.12, 6.71, 7.75, 8.20.

N-Tricyclo[6.2.2.0^{2,7}]dodec-3-one-9-ylidenepyrrolidinium Perchlorate (7).—A solution of 9.6 g (0.1 mole) of 2-cyclohexenone, 17.1 g (0.1 mole) of pyrrolidine perchlorate, and 1 drop of pyrrolidine in 250 ml of benzene was heated under reflux with stirring for 4.5 hr under a Dean–Stark trap to collect the theoretical 1.8 ml of water liberated in the reaction. The benzene was decanted from the crude semisolid **N,N′-tricyclo[6.2.2.0^{2,7}]-dodeca-3,9-diylidenepyrrolidinium diperchlorate**, which was then boiled in 200 ml of ethanol for 45 min to dissolve impurities. The ethanol was decanted, and the solid was boiled in about 100 ml of water for about 2 min. The hot solution was decanted from the small amount of insoluble material and allowed to cool. Colorless needles formed with yellow oily matter as their nuclei, and this material was filtered and again dissolved in boiling water and treated with Darco. After the hot solution was filtered, the water was completely removed *in vacuo*. The resulting solid was dissolved in nitromethane, treated with Darco, and filtered. Colorless to ivory needles precipitated on the addition of ethanol–ether: yield 7.2 g (42%); mp 230.5–232.5°; $\nu_{\max}^{\text{Nujol}}$ 1703 (C═O), 1675 cm^{-1} (C═N$^+$), and no band for N$^+$—H. The nmr spectrum (TFA–TMS) showed signals at τ 5.95, large multiplet at τ 6.73 to 7.48, 7.69, and 8.00.

Anal. Calcd for $C_{16}H_{24}ClNO_5$: C, 55.57; H, 7.00; N, 4.05. Found: C, 55.45; H, 7.16; N, 4.26.

N-Tricyclo[6.2.2.0^{2,7}]dodec-3-ol-9-ylpyrrolidine Perchlorate (9).—A solution of 0.450 g (1.3 mmoles) of N-tricyclo[6.2.2.0^{2,7}]-dodec-3-one-9-ylidenepyrrolidinium perchlorate and 0.450 g (118 mmoles) of sodium borohydride in 220 ml of 2-propanol was refluxed with stirring for 17 hr. The solvent was removed *in vacuo;* the solids were dissolved in aqueous sodium hydroxide and extracted with ether. The ether solution was dried over magnesium sulfate and acidified with 1:1 ethanol–perchloric acid. The colorless solid, obtained in 68% yield (0.310 g), was recrystallized from ethanol-ether, leading to fine colorless needles: mp 221–222°; $\nu_{\max}^{\text{CHCl}_3}$ 3530 (O–H), *ca.* 3030 cm^{-1} (N$^+$—H) (partially hidden); nmr τ values (TFA–TMS), 6.17, 6.67, 7.21, 7.49, 7.80, 8.23, 8.45, 8.62.

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(44) K. C. Brannock, A. Bell, R. D. Burpitt, and C. A. Kelley, *ibid.*, **26**, 625 (1961).

(45) We are very grateful to Professor P. E. Eaton of the University of Chicago for providing us with a preprint of his article on the photodimers of cyclohexenone. See also ref 46 and 47.

(46) P. E. Eaton, *J. Am. Chem. Soc.*, **84**, 2344 (1962).

(47) P. E. Eaton, *ibid.*, **84**, 2454 (1962).

(48) D. Valentine, N. J. Turro, Jr., and G. S. Hammond [*ibid.*, **86**, 5202 (1964)] have also prepared these dimers by the Eaton directions.

(49) We wish to thank Mr. Josef Nemeth and his associates for the microanalyses and molecular weight determinations, and Mr. Dick Johnson and his associates for the nmr and infrared spectra. The nmr spectra were obtained with a Varian Associates Model A-60 spectrometer. The chemical shifts were measured using tetramethylsilane as an internal standard (τ 10). Infrared spectra were obtained with a Perkin-Elmer Model 521 infrared spectrometer. Molecular weight determinations were carried out with a Mechrolab, Inc., vapor pressure osmometer, Model 301A. The melting points reported herein are corrected.

Anal. Calcd for $C_{16}H_{28}ClNO_5$: C, 54.93; H, 8.07; N, 4.00. Found: C, 54.99; H, 8.25; N, 4.16.

Di-N,N′-Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium Diperchlorate (1) from N-Tricyclo[6.2.2.0^{2,7}]dodec-3-on-9-ylidenepyrrolidinium Perchlorate (7).—In 150 ml of benzene were placed 0.844 g (2.44 mmoles) of **7**, 0.423 g (2.47 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine. The mixture was heated under reflux with stirring under a Dean–Stark trap for 9 hr. The hot benzene solution was filtered, and the solid was crystallized from nitromethane–ethanol–ether. Treatment of the material with Darco afforded 0.873 g (72%) of product which, after an additional recrystallization, yielded analytically pure material, mp 267–269° dec, whose infrared and nmr spectra were identical with those obtained from the product of pyrrolidine perchlorate and 2-cyclohexenone. (The melting point of **1** is apparently dependent upon the number and conditions of recrystallization. The possibility that varying isomeric mixtures are present, may, at least in part, account for this.)

Tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (10).—In 100 ml of water containing 0.6 g (15.0 mmoles) of sodium hydroxide was placed 4.0 g (11.6 mmoles) of crude N-tricyclo[6.2.2.0^{2,7}]dodec-3-one-9-ylidenepyrrolidinium perchlorate (**7**), and the solution was overlayered with 100 ml of ether. This mixture was stirred at room temperature for 17 hr. The aqueous layer was separated and extracted with ether and methylene chloride. The organic solutions were combined and the solvents were removed *in vacuo*. The residual oil was chromatographed on 150 g of activated acid-washed alumina with 10% ethanol in ether. The solvent was removed *in vacuo* to afford 2.0 g (90%) of an oil which slowly solidified on standing. A 1-g portion of this crude product was recrystallized five times from hexane (collecting two crops) to yield 0.5 g (45%) of colorless flakes: mp 58.5–59.5°; $\nu_{\max}^{\mathrm{CCl_4}}$ 1727, 1706 cm^{-1} (C=O). The nmr spectrum (CCl_4–TMS) showed signals at τ 7.40, 7.90, and 8.21.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39; mol wt, 192.3. Found: C, 74.97; H, 8.46; mol wt, 183.8 (osmometric in benzene).

Prepared in the usual manner in 57% yield as a colorless solid insoluble in all common solvents tried, the **bissemicarbazone** was purified by digesting in a variety of solvents, mp 282–284°.

Anal. Calcd for $C_{14}H_{22}N_6O_2$: C, 54.89; H, 7.24; N, 27.43. Found: C, 54.67; H, 7.44; N, 26.30.

Tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (10) from 1.—A solution of 3.27 g (6.7 mmoles) of di-N,N′-tricyclo[6.2.2.0^{2,7}]-dodeca-3,9-diylidenepyrrolidinium diperchlorate (**1**) and 0.6 g (15 mmoles) of sodium hydroxide in 150 ml of water overlayered with 100 ml of ether was stirred at room temperature for 2 days. The layers were separated, and the aqueous layer was extracted further with ether. The ether solutions were combined, dried, and concentrated *in vacuo*. The residual oil was chromatographed on 100 g of Woelm neutral activity I alumina with 10% ethanol in ether to yield 0.9 g (70%) of product as an oil. The infrared and nmr spectra were identical with those of the diketone obtained from N-tricyclo[6.2.2.0^{2,7}]dodec-3-on-9-ylidenepyrrolidinium perchlorate (**7**). (In most instances tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione was obtained initially as an oil which could be crystallized by treatment with hexane.)

Di-N,N′-Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium Diperchlorate (1) and N-Tricyclo[6.2.2.0^{2,7}]dodec-3-on-9-ylidenepyrrolidinium Perchlorate (7) from Tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (10).—In 60 ml of benzene were placed 0.17 g (0.885 mmole) of tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione, 0.15 g (0.885 mmole) of pyrrolidine perchlorate, and 1 drop of pyrrolidine. The mixture was refluxed for 20 hr under a Dean–Stark trap. The solution was cooled to room temperature; the solid was filtered and washed in 20 ml of ethanol. The insoluble colorless salt was recrystallized from nitromethane–ether to afford 0.10 g (45% based on theory for this product) of **1** with the correct analysis: mp 262–264° dec, infrared spectrum identical with that of authentic sample. The decomposition point observed varies with the number of recrystallizations in addition to possible changes with isomer composition.

The benzene solution was combined with the ethanol washings, and the solvents were removed *in vacuo* to yield 0.11 g (36% based on theory for this compound) of crude **7**, which was recrystallized twice from nitromethane–ether. The colorless powder had mp 221–224° dec, mmp (with authentic sample of salt) 221–224° dec. Crystal form and melting point varied somewhat with recrystallization conditions. The compound had the correct analysis for $C_{16}H_{24}ClNO_5$ (see above).

4,10-Dipiperonylidenetricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione.—In 70 ml of ethanol were placed 0.6 g (3.1 mmoles) of tricyclo-[6.2.2.0^{2,7}]dodecane-3,9-dione (**10**), 4.2 g (27.5 mmoles) of freshly recrystallized piperonal, and 5 ml of 5 *N* sodium hydroxide. The solution was stirred at room temperature for 24 hr, and then the tan colored solid was collected. Crystallization from 400 ml of ethanol–water (10:1) yielded 0.75 g (54%) of light yellow product. An additional recrystallization from 2:1 ethanol–water afforded pure material, mp 212–215°, $\nu_{\max}^{\mathrm{Nujol}}$ 1682 cm^{-1} (broad), $\lambda_{\max}^{\mathrm{EtOH}}$ 331 mμ (log ϵ 4.56). The nmr spectrum showed a ratio of the total of benzylidene, methylenedioxy, and aromatic protons to the rest of the hydrogens of 1:1.06.

Anal. Calcd for $C_{28}H_{24}O_6$: C, 73.67; H, 5.30. Found: C, 73.40; H, 5.44.

2,6-Dipiperonylidenecyclohexanone was prepared as described above in 70% yield as a yellow powder and recrystallized from chloroform–methanol: mp 188–191°, $\nu_{\max}^{\mathrm{Nujol}}$ 1658 cm^{-1}, $\lambda_{\max}^{\mathrm{EtOH}}$ 370 mμ (log ϵ 4.37).

Anal. Calcd for $C_{22}H_{18}O_5$: C, 72.92; H, 5.01. Found: C, 72.99; H, 5.03.

Deuterium Exchange with Tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione (10).—To 0.18 g of analytically pure tricyclo[6.2.2.0^{2,7}]-dodecane-3,9-dione was added 3 ml of deuterium oxide (99.7% deuterium) with a trace of sodium hydroxide. The mixture was warmed to melt the insoluble diketone, after which the solvent was removed *in vacuo* with heating. This process was repeated three times after which the material was recrystallized from hexane for analysis. The whole process was repeated twice more, yielding the following analyses. Estimated error is ±1% relative or 0.25 atom %.

No. of treatments	D, atom %	D/molecule
3	22.65	3.6
6	24.60	3.9
9	30.3	4.85

Wolff–Kishner Reduction of Tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione Bissemicarbazone.—In a combustion tube were placed 1.25 g (4.06 mmoles) of tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione bissemicarbazone and 1.8 g of sodium in 28 ml of ethanol. The tube was sealed and heated to 200–205° for 17 hr. The cooled contents of the tube were poured into 200 ml of water; the water was extracted four times with 75-ml portions of ether. The combined ether solutions were washed with dilute hydrochloric acid and dried over magnesium sulfate, and the ether was removed *in vacuo*. The crude yield of **tricyclo[6.6.2.0^{2,7}]dodecane (11)** was 0.50 g (75%). The material was carefully distilled over sodium in a Hickman still to yield 0.18 g of pure product: bp 125–135° (bath temperature) (17–20 mm), $n^{24}\mathrm{D}$ 1.5083. Vapor phase chromatography on a 2-ft column of 20% tri-*o*-cresyl phosphate on firebrick at 150° shows a 10% minor fraction of lower retention time. Both major and minor fractions had the same retention time as those found for the hydrocarbon obtained by the Diels–Alder route (see below). The infrared spectrum was identical with that of the hydrocarbon obtained *via* the Diels–Alder route. The nmr spectrum ($CDCl_3$–TMS) showed peaks at τ 8.45, shoulder τ 8.57, multiplet to peak at τ 8.75, 8.90 (sh) [lit[8] bp 110–111° (16 mm), $n^{20}\mathrm{D}$ 1.5081].

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.51; H, 12.19.

Tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (12).[35,36]—In a sealed tube 30.8 g (0.308 mole) of 80% 1,3-cyclohexadiene with a trace of hydroquinone was heated for 24 hr at 200°. The product was distilled over sodium: bp 103–106° (13 mm); yield 7.35 g (30%); $n^{22.5}\mathrm{D}$ 1.5269; $\nu_{\max}^{\mathrm{film}}$ 1650 (w) (C=C), 3070, 708 cm^{-1} (*cis* CH=CH) (Infracord); $n^{22}\mathrm{D}$ 1.5260; $\nu_{\max}^{\mathrm{film}}$ 1656, 710, 3067 cm^{-1}) [lit.[8] bp 100–102° (9 mm)].

Reduction of 12.—In 100 ml of ethanol were placed 7.33 g (46 mmoles) of tricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (**12**) and 0.73 g of platinum oxide. The mixture was hydrogenated at room temperature and atmospheric pressure until hydrogen absorption ceased (4.5 hr). The catalyst was removed by filtration and the ethanol was evaporated. The residue was distilled over sodium to yield 6.35 g (83%) of **tricyclo[6.2.2.0^{2,7}]dodecane (11)**: bp 111–113° (15 mm); $n^{23.5}\mathrm{D}$ 1.5070; $\nu_{\max}^{\mathrm{CHCl_3}}$ 2650 (w), 1465, 1308 (w), 1275 (w), 1140 (broad), 978 (w), 868 (w), 835 (w) cm^{-1} [lit.[8] bp 110–111° (16 mm); $n^{20}\mathrm{D}$ 1.5081]. The nmr spectrum ($CDCl_3$–TMS) showed peaks at τ 8.45, multiplet to peak at τ 8.77, and 8.90 (sh). Vapor phase chromatography on a 2-ft column of 20% tri-*o*-cresyl phosphate on firebrick at 150° showed a 7% minor fraction with lower retention time than the main fraction.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.51; H, 12.16.

Isomeric Tricyclo[6.2.2.0^{2,7}]dodecanes.—Vapor phase chromatography of the saturated hydrocarbon obtained by the Diels–Alder route on a 2-ft column of tri-*o*-cresyl phosphate on firebrick at 150° showed a major peak of retention time 351 sec and a minor peak, comprising 7% of the total hydrocarbon, of retention time 245 sec. Similar chromatography of the saturated hydrocarbon obtained from tricyclo[6.2.2.0^{2,7}]dodecane-3,9-dione bissemicarbazone showed the identical two peaks, the only difference being the relative amounts of the minor component, which varied from 10 to 24% of the total hydrocarbon.

Chromatography on a 3 ft × $^3/_8$ in. preparative column of tri-*o*-cresyl phosphate at 150° afforded the major component, *cis*-tricyclo[6.2.2.0^{2,7}]dodecane, 96–98% pure as shown by vpc after redistillation over sodium: $n^{26.5}D$ 1.5073; $\nu_{max}^{CHCl_3}$ 2935, 2870, 1480, 1469, 1455 cm^{-1}; nmr τ values ($CDCl_3$–TMS), 8.46, 8.52–8.81, 8.94.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.94; H, 12.18.

The minor component, *trans*-tricyclo[6.2.2.0^{2,7}]dodecane, was obtained, after distillation over sodium, 95–97% pure as shown by vpc: $\nu_{max}^{CHCl_3}$ 2928, 2855, 1465 (sh), 1451, 1440 (sh) cm^{-1}. A second sample of 89% pure *trans* isomer had nmr τ values ($CDCl_3$–TMS) of 7.86–8.14, 8.25–8.55, 8.60–8.88, and 8.92–9.08.

Anal. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27. Found: C, 87.87; H, 12.35.

Reaction of 2-Cyclohexenone and Pyrrolidine Perchlorate in Ethanol at Room Temperature.—In 75 ml of ethanol were placed 3.8 g (39.6 mmoles) of 2-cyclohexenone, 6.8 g (39.6 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine. The solution was stirred at room temperature for 48 hr, during which time the solution turned dark red-brown in color and a semisolid oil precipitated. The ethanol was decanted to yield 3.6 g of this semisolid. This material was worked up as described for the preparation of the dimeric product. The material was considerably less pure than that obtained by the usual refluxing in benzene method, and after extensive purification, 1.0 g (10%) of fairly pure material was obtained. Its infrared spectrum was identical with the spectrum of authentic di-N,N′-tricyclo-[6.2.2.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium diperchlorate (1).

Reaction of Pyrrolidine with 2-Cyclohexenone.—A solution of 3.7 g (38 mmoles) of 2-cyclohexenone, 2.7 g (38 mmoles) of pyrrolidine, and about 0.1 g of *p*-toluenesulfonic acid in 200 ml of benzene was heated at reflux under nitrogen for 5 hr, using a Dean–Stark trap. A total of 0.6 ml of water was collected (86%). The benzene was removed *in vacuo* to afford an unstable oil which could not be distilled without excessive polymerization and decomposition. Consequently, the crude product, presumed to contain **di-3,9-N,N′-dipyrrolidyltricyclo[6.2.2.0^{2,7}]dodeca-3,9-diene (5)**, was stirred with 5 g of sodium hydroxide in 150 ml of water for 2.5 hr. The solution was acidified and extracted with ether. After the solution was dried, the ether was removed *in vacuo* to yield 1.9 g (51%) of crude **tricyclo-[6.2.2.0^{2,7}]dodecane-3,9-dione (10)**, judged by infrared and nmr spectra, but difficulty was encountered in purification. The pyrrolidine-2-cyclohexenone condensation in the absence of the acid catalyst gave approximately the same results as described above.

An attempted reaction of 2-cyclohexenone in the presence of triethylamine under similar conditions led only to the recovery of starting ketone as evidenced by infrared spectra.

2-(3′-Oxocyclohexyl)cyclohex-2-enone (13).—To 200 ml of 10% aqueous sodium hydroxide was added 5.0 g (0.052 mole) of 2-cyclohexenone. The mixture was stirred at room temperature for 12 hr. The insoluble product was extracted into ether, the ether solution was dried, and after the ether was removed, the product was distilled as a colorless, fairly viscous oil, bp 148–154° (1.8 mm), $n^{25}D$ 1.5230, yield 3.2 g (64%). An extension of the reaction time for an additional 24 hr did not affect the product composition. The structure assigned to the product predominating was based on the following spectral evidence: $\nu_{max}^{CHCl_3}$ 1706 (C=O), 1668 cm^{-1} (conjugated C=O); λ_{max}^{EtOH} 233 and 285 mμ (ϵ 8000 and 112, respectively); nmr signals ($CDCl_3$–TMS) at τ 3.29 (t, J = 3.5 cps, 0.93H, C=C*H*), 7.07, 7.61, 7.96, 8.04, 8.17, 8.29, 8.43.

Anal. Calcd for $C_{12}H_{16}O_2$: C, 74.97; H, 8.39. Found: C, 75.37; H, 8.48.

N-Cyclohexylpyrrolidine Perchlorate.[50]—A solution of 7.1 g (27.3 mmoles) of N-cyclohexylidenepyrrolidinium perchlorate and 3.5 g (92 mmoles) of sodium borohydride in 200 ml of 2-propanol was heated under reflux with stirring for 7 hr. The solvent was removed *in vacuo*, and the solid was dissolved in aqueous sodium hydroxide. The solution was extracted with ether. The ether solution was dried over magnesium sulfate and then acidified with 1:1 ethanol–perchloric acid to yield 2.9 g (41%) of amine salt. The product was recrystallized as long, colorless needles from ethanol–ether: mp 120–120.5°; ν_{max}^{Nujol} 3150 cm^{-1} (N$^+$–H) (Infracord).

Anal. Calcd for $C_{10}H_{20}ClNO_4$: C, 47.33; H, 7.95; N, 5.52. Found: C, 47.40; H, 8.04; N, 5.51.

N-(3,5,5-Trimethyl-2-cyclohexenylidene)pyrrolidinium Perchlorate (2).—An ethereal solution of 10 g (52 mmoles) of 1-N-pyrrolidyl-3,5,5-trimethyl-1,3-cyclohexadiene[19,51] was acidified with 1:1 ethanol–perchloric acid to yield 15 g (98%) of the iminium salt, mp 117–118°, which was recrystallized from ethanol–ether as fine colorless needles, mp 108–109°, $\nu_{max}^{CHCl_3}$ 1610 cm^{-1}, $\lambda_{max}^{CH_3CN}$ 268 mμ (ϵ 19,800); the nmr spectrum (TFA–TMS) showed the olefinic proton at τ 3.49. An attempt to prepare this salt by direct condensation of isophorone and pyrrolidine perchlorate failed.

Anal. Calcd for $C_{13}H_{22}ClNO_4$: C, 53.51; H, 7.60; N, 4.80. Found: C, 53.63; H, 7.68; N, 5.07.

N-(3,5,5,-Trimethyl-2-cyclohexenyl)pyrrolidine Perchlorate.—A solution of 2.0 g (6.9 mmoles) of N-(3,5,5-trimethyl-2-cyclohexenylidene)pyrrolidinium perchlorate and 1.2 g (31 mmoles) of sodium borohydride in 200 ml of 2-propanol was heated at reflux with stirring for 24 hr. The solvent was removed *in vacuo* and the solid residue was dissolved in aqueous sodium hydroxide. The basic solution was extracted with ether; the ethereal solution was dried over magnesium sulfate and then acidified with 1:1 perchloric acid–ethanol, yielding 1.72 g (85%) of colorless solid. The product was recrystallized from ethanol as colorless needles: mp 181–182°; $\nu_{max}^{CHCl_3}$ 1667 (C=C), 3070 cm^{-1} (N$^+$–H); the nmr spectrum ($CDCl_3$–TMS) showed the olefinic proton at τ 4.55.

Anal. Calcd for $C_{13}H_{24}ClNO_4$: C, 53.15; H, 8.23; N, 4.77. Found: C, 53.32; H, 8.38; N, 4.84.

Photodimers of 2-Cyclohexenone (14 and 16).—2-Cyclohexenone was freed of alcoholic impurities by treatment with α-naphthyl isocyanate, followed by filtration, extraction, and distillation. The directions provided by Eaton[45-47] were followed for the irradiation of the pure 2-cyclohexenone under nitrogen with a Hanovia 450-w high-pressure mercury lamp and for the chromatographic separation of the two isomeric products: ***cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,9-dione (14)**, colorless needles from hexane, mp 54.5–55.5° (lit.[45] mp 54–55°); and ***cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]dodecane-3,12-dione (16)**, colorless flakes from hexane, mp 79–80° (lit.[45] mp 80.5–81.5°).

Di-N,N′-*cis,trans,cis*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,9-diylidenepyrrolidinium Diperchlorate (15).—In 85 ml of benzene were placed 0.8 g (4.16 mmoles) of *cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]-dodecane-3,9-dione (14), 1.5 g (8.7 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine. The reaction mixture was heated under reflux for 17 hr and worked up as described above to yield 1.45 g (70%) of product which, after recrystallization from nitromethane–ether, was a colorless powder, mp 290–291° dec, ν_{max}^{Nujol} 1650 cm^{-1} (C=N$^+$). Nmr signals (TFA–TMS) occurred at τ 6.00, 6.40, 7.00, 7.71, and 7.86.

Anal. Calcd for $C_{20}H_{32}Cl_2N_2O_8$: C, 48.10; H, 6.46; N, 5.61. Found: C, 47.83; H, 6.43; N, 5.66.

Di-N,N′-*cis,trans,cis*-Tricyclo[6.4.0.0^{2,7}]dodeca-3,12-diylidenepyrrolidinium Diperchlorate (17).—In 85 ml of benzene were placed 0.8 g (4.16 mmoles) of *cis,trans,cis*-tricyclo[6.4.0.0^{2,7}]-dodecane-3,12-dione (16), 1.5 g (8.7 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine. The reaction and product isolation were carried out by the general procedure to yield 1.5 g (73%) of product. Recrystallization from nitromethane–ether yielded pure material as a colorless powder, mp 276–277° dec, ν_{max}^{Nujol} 1647 cm^{-1} (C=N$^+$). The nmr spectrum (TFA–TMS) had signals at τ 5.79, 5.90, 6.32, 6.95, 7.70, and 8.04.

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(50) N. J. Leonard and B. Müller, unpublished results.

(51) S. Hünig and H. Kahanek, *Ber.*, **90**, 238 (1957).

Anal. Calcd for $C_{20}H_{32}Cl_2N_2O_8$: C, 48.10; H, 6.46; N, 5.61. Found: C, 48.26; H, 6.60; N, 5.66.

Di-N,N'-*cis,trans,cis*-Tricyclo[5.3.0.0^{2,6}]deca-3,8-diylidenepyrrolidinium Diperchlorate.—This material was prepared in the usual manner from 1.37 g (8.35 mmoles) of *cis,trans,cis*-tricyclo-[5.3.0.0^{2,6}]decane-3,8-dione,[46] 2.86 g (16.7 mmoles) of pyrrolidine perchlorate, and 1 drop of pyrrolidine in 91% yield. Purification was effected by solution in nitromethane, treatment with Darco, followed by crystallization induced by the addition of ethanol. The colorless powder had mp >315° (the crude material *explodes* at about 315°); ν_{max}^{Nujol} 1710 cm^{-1} ($C{=}N^+$); nmr τ values (TFA-TMS) at 5.95, 6.30, 6.55, 6.69, 7.69.[52]

Anal. Calcd for $C_{18}H_{28}Cl_2N_2O_8$: C, 46.25; H, 5.99; N, 5.95. Found: C, 45.93; H, 6.26; N, 5.75.

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[52] Nmr spectral curves for the compounds reported herein are given in the Ph.D. Thesis of W. J. Musliner, University of Illinois, 1965.

The Chemistry of Carbanions. XI. Michael Reactions with 2-Methylcyclopentanone and 2-Methylcyclohexanone[1a]

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The reaction of 2-methylcyclopentanone with methyl acrylate and the reactions of 2-methylcyclohexanone with methyl acrylate, methyl propiolate, and the methyl *cis*- and *trans*-3-chloroacrylates have been studied. The predominant formation of 2,2-disubstituted cycloalkanones as Michael products in certain of these reactions appears to be attributable to a combination of two factors. First, the positions of the relevant enolate anion equilibria favor the 2,2 isomer. Secondly, the minor product, the 2,6 isomer **5** from 2-methylcyclohexanone, is converted to dialkylated products (or other products) more rapidly than the 2,2 isomer **2** with the result that the proportion of 2,6 isomer **5** in the monoalkylated product decreases as the reaction proceeds. The initial Michael adducts **2a** and **5a** have been shown not to be interconverted under the Michael reaction conditions.

Earlier studies[2] of the Michael addition[3] of 2-methylcyclohexanone (**1**) to methyl acrylate in the presence of potassium *t*-butoxide and *t*-butyl alcohol indicated that the only monoalkylated product formed in appreciable quantity was the 2,2 isomer **2**. In the present study, both this reaction and the corresponding addition of 2-methylcyclopentanone (**3**) to methyl acrylate have been examined. The 2,6 stereoisomers **5** were described previously[2] and the 2,5 isomer **6** (a mixture of *cis* and *trans* isomers) has been obtained by the reaction scheme indicated in Chart I. Appropriate physical measurements (see Experimental Section) on the crude reaction products demonstrated that the crude monoalkylated product from the cyclopentanone **3** was largely (*i.e.*, >90%), if not exclusively, the 2,2 isomer **4a**. The monoalkylated product from 2-methylcyclohexanone (**1**) contained the 2,2 isomer **2a** (93%) and the 2,6 isomer **5a** (7%); when this latter reaction was run with 1,2-dimethoxyethane (DME) as the solvent, the monoalkylated product was composed of 88% of **2a** and 12% of **5a**. In all of these reactions higher molecular weight products were present which are believed to be dialkylated (*e.g.*, **9** from **1**) or trialkylated materials.

In seeking an explanation for the structural specificity of these Michael reactions, it was of interest to consider the equilibrium positions and the relative rates of formation of the enolate anions **10** and **11** derived from ketones **1** and **3**. For both of these cyclic ketones, the relative rates of formation of the isomeric enolate anions (*e.g.*, **10a** and **10b** from **1**) are approximately equal.[4] Consequently, any argument based on a rate-limiting enolate anion formation does not account for the structural specificity observed. The equilibrium concentrations for these enolate anions **10** and **11** are summarized in Chart II. The values for enolate anions generated with triphenylmethyl potassium in 1,2-dimethoxyethane (DME) were described previously[4] and the corresponding values for anions **10** generated from potassium *t*-butoxide were obtained by quenching the solutions in excess acetic anhydride to form the enol acetates **12** and **13**. Because of our previously noted[4a] inability to resolve these enol acetates, **12** and **13**, by gas chromatography, it was necessary to estimate the composition of the mixture from its nmr spectrum. Of incidental interest are the yields of enol acetates **12** and **13** which were obtained. The solution prepared from equimolar amounts of the ketone **1** and potassium *t*-butoxide in *t*-butyl alcohol gave 13–15% of the enol acetate mixture; the corresponding reaction in 1,2-dimethoxyethane yielded 50–60% of the enol acetate mixture. These yield data provide an estimate of the fraction of the ketone **1** which has been converted to its enolate anions by potassium *t*-butoxide in *t*-butyl alcohol and in 1,2-dimethoxyethane. It is clear that a larger fraction of the ketone **1** is present as its enolate anions in 1,2-dimethoxyethane solution.[5]

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[2] H. O. House and M. Schellenbaum, *J. Org. Chem.*, **28**, 34 (1963), and references therein.

[3] E. D. Bergmann, D. Ginsberg, and R. Pappo, *Org. Reactions*, **10**, 179 (1959).

[4] (a) H. O. House and V. Kramar, *J. Org. Chem.*, **28**, 3362 (1963); (b) H. O. House and B. M. Trost, *ibid.*, **30**, 1341 (1965). A typographical error resulted in interchanging the formulas for the 2-methylcyclopentanone enolate anions in Table I of this reference. For the correction, see Additions and Corrections, *ibid.*, **30**, 4395 (1965).

[5] It should be noted that, while the commercially available *alcohol-free* potassium *t*-butoxide (and also lithium *t*-butoxide) is readily soluble in 1,2-dimethoxyethane, the corresponding alkoxides (both potassium and lithium) are much less soluble when 1 equiv of *t*-butyl alcohol is added. As a result the potassium *t*-butoxide prepared by reaction of potassium with excess *t*-butyl alcohol in the usual manner followed by distillation of the solvent is not readily soluble in 1,2-dimethoxyethane. Apparently, the 1:1 complex of potassium *t*-butoxide and *t*-butyl alcohol is distinctly less soluble in 1,2-dimethoxyethane than is the pure metal alkoxide. For discussion and other examples, see ref 6 and C. W. Kamienski and D. H. Lewis, *J. Org. Chem.*, **30**, 3498 (1965).