Truxanes. I. Preparation and Characterization of Indene Photodimers and Related Compounds[1a]

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The structure of indene photodimer 9, a new truxane, was established and the remaining unknown truxones were prepared. These compounds are of interest as possible precursors for the dibenzo derivatives of 3, a novel 10-π-electron system.

In striking contrast to the high lability of parent cyclobutadiene, predicted initially on theoretical grounds[2–8] and subsequently demonstrated experimentally,[9–13] a number of polybenzenoid cyclobutadienes have been successfully synthesized[14–20] and found to display appreciable stability as anticipated from simple Hückel theory.[3] On the other hand, nonbenzenoid polycyclic systems incorporating fully trigonal four-membered rings are not known.

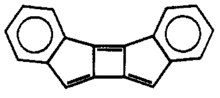
One potentially stable candidate in the series of symmetrically annellated, nonbenzenoid cyclobutadienes is tricyclo[5.3.0.0^{2,6}]decapentaene[18] (**3**), which, unlike the two lower members of the family **1** and **2**, ought not to be subject to prohibitively high skeletal strain.[19] Moreover, **3** satisfies the conditions for aromatic stability since it contain $4n + 2$ π electrons, all of which are peripheral, and is predicted to possess a totally symmetric ground state.

We carried out Hückel calculations on **3** and the dibenzo derivatives **4** and **5**. Simple inspection of the data, collected in Table I, reveals that all three systems are predicted to possess reasonably low free valencies, appreciable delocalization energies, and such bond orders as to suggest considerable peripheral delocalization of π electrons. Inspection of the MO energy levels of these systems reveals, however, that the *lowest* vacant MO is slightly antibonding in **4** and **5** and nonbonding in **3**. This piece of information casts some doubt concerning the anticipated stability of **3**. In fact, the nonbonding nature of the *lowest* vacant MO is reminiscent of the π-electronic arrangement in the elusive pentalene ($\mathrm{DE}_{\mathrm{HMO}} = 2.46\beta$),[21] a $4n$ system!

1

2

3



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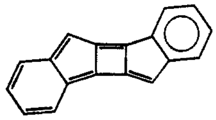

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The difference in stability between **4** and **5** is of a more subtle nature and cannot be predicted with any degree of confidence from the HMO data. Examination of the energies of the highest occupied and lowest unoccupied MO's of these systems, however, is instructive. For two related systems such as **4** and **5**, it may be said that the absolute value of the difference in energy between the respective highest occupied MO's should be a measure of their relative stability toward oxidation, while the energy difference between their lowest unoccupied MO's should be indicative of their relative tendencies to undergo reduction. On this basis, system **4** is predicted to be more stable than **5** by 0.15β toward oxidation and by 0.10β toward reduction. Simple resonance considerations also point to **4** as the more stable isomer, since in this the basic nonbenzenoid unit is capable of independent existence, while in **5** this unit can only exist at the expense of benzenoid resonance.

Results and Discussion

Encouraged by the predictions that **4** would be capable of more than precarious independent existence we directed our attention to the synthesis of appropriate precursors, namely the two possible isomeric *syn*-truxones **6** and **7** and the corresponding truxanes **8** and **9**. At the outset of this investigation, a survey of the literature revealed that none of these compounds (**6** through **9**) had been reported previously.

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[1] (a) The material presented in this paper has been taken from the thesis of A. G. Anastassiou, submitted in partial fulfillment of the requirements for the Ph.D. degree at Yale University, 1963. (b) To whom requests for reprints should be addressed at the Department of Chemistry, Louisiana State University in New Orleans, New Orleans, La.

[2] D. P. Craig, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers Inc., New York, N. Y., 1959, pp 29–37.

[3] H. E. Simmons and A. G. Anastassiou, "Cyclobutadiene and Related Compounds," M. P. Cava and M. J. Mitchell, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 12.

[4] G. W. Wheland, *J. Chem. Phys.*, **2**, 474 (1934).

[5] H. E. Simmons, unpublished calculations; see ref 3.

[6] M. J. S. Dewar and G. J. Gleicher, *J. Amer. Chem. Soc.*, **87**, 685 (1965).

[7] M. J. S. Dewar and G. J. Gleicher, *ibid.*, **87**, 3255 (1965).

[8] L. C. Snyder, Symposium on Molecular Structure and Spectroscopy, Paper B-4, The Ohio State University, Columbus, Ohio, 1960; Paper B-7 (1961).

[9] W. Baker and J. F. W. McOmie, "Non-Benzenoid Aromatic Compounds," D. Ginsburg, Ed., Interscience Publishers Inc., New York, N. Y., 1959, Chapter II; M. P. Cava and M. J. Mitchell, "Cyclobutadiene and Related Compounds," M. P. Cava and M. J. Mitchell, Ed., Academic Press Inc., New York, N. Y., 1967, Chapter 1.

[10] Although a number of ingenious experiments[11–13] designed to generate cyclobutadiene have led to dimers and other cycloadducts, the existence of the free molecule for any length of time has as yet to be demonstrated conclusively.

[11] R. Criegee and G. Louis, *Chem. Ber.*, **90**, 417 (1957).

[12] P. S. Skell and R. J. Petersen, *J. Amer. Chem. Soc.*, **86**, 2530 (1964).

[13] L. Watts, J. D. Fitzpatrick, and R. Pettit, *ibid.*, **87**, 3253 (1965).

[14] W. C. Lothrop, *ibid.*, **63**, 1187 (1941).

[15] M. P. Cava and J. F. Stucker, *ibid.*, **77**, 6022 (1955).

[16] F. R. Jensen and W. E. Coleman, *Tetrahedron Lett.*, No. 20, 7 (1959).

[17] R. F. Curtis and G. Viswanath, *Chem. Ind.* (London), 1174 (1954).

[18] J. W. Barton, *J. Chem. Soc.*, 5161 (1964).

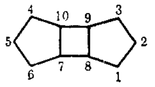
[19] J. W. Barton, A. M. Rogers, and M. E. Barney, *ibid.*, 5537 (1965).

[20] M. P. Cava, B. Hwang, and J. P. Van Meter, *J. Amer. Chem. Soc.*, **85**, 4032 (1963).

[21] No quantitative significance should be attached to these values, which are presented merely to illustrate the line of reasoning.

Table I

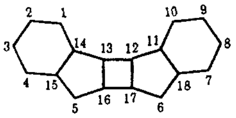
HMO Indices[a]



r,s	P_{rs}	r	F_r	q_r
1, 2	0.626	1	0.463	1.163
1, 8	0.645	2	0.480	0.908
7, 8	0.578	7	0.275	0.886
7, 10	0.239			

$\epsilon_1 = \alpha + 2.56\beta_0$
$\epsilon_2 = \alpha + 1.73\beta_0$
$\epsilon_3 = \epsilon_4 = \alpha + \beta_0$
$\epsilon_5 = \alpha + 0.41\beta_0$
$\epsilon_6 = \alpha$

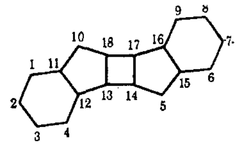
DE = $3.40\beta_0$



r,s	P_{rs}	r	F_r	q_r
1, 2	0.680	1	0.453	0.963
2, 3	0.639	2	0.414	1.023
3, 4	0.676	3	0.417	0.977
4, 15	0.604	4	0.452	1.012
15, 5	0.464	15	0.136	0.994
5, 16	0.763	5	0.505	1.102
16, 17	0.428	16	0.249	0.994
16, 13	0.293	13	0.306	0.886
13, 14	0.463	14	0.142	1.049
14, 1	0.599			
13, 12	0.670			
14, 15	0.528			

$\epsilon_1 = \alpha + 2.62\beta_0$
$\epsilon_2 = \alpha + 2.21\beta_0$
$\epsilon_3 = \alpha + 1.81\beta_0$
$\epsilon_4 = \alpha + 1.38\beta_0$
$\epsilon_5 = \alpha + 1.33\beta_0$
$\epsilon_6 = \alpha + 1.12\beta_0$
$\epsilon_7 = \alpha + 1.00\beta$
$\epsilon_8 = \alpha + 0.60\beta_0$
$\epsilon_9 = \alpha + 0.39\beta_0$
$\epsilon_{10} = \alpha - 0.15\beta_0$

DE = $6.92\beta_0$

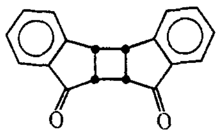


r,s	P_{rs}	r	F_r	q_r
1, 2	0.705	1	0.455	1.033
2, 3	0.604	2	0.423	0.960
3, 4	0.713	3	0.415	1.042
4, 12	0.556	4	0.463	0.948
12, 13	0.555	12	0.138	1.065
13, 14	0.564	13	0.357	0.828
13, 18	0.256	18	0.238	0.962
18, 10	0.674	10	0.520	1.188
10, 11	0.538	11	0.139	0.974
11, 12	0.483			
11, 1	0.572			

$\epsilon_1 = \alpha + 2.62\beta_0$
$\epsilon_2 = \alpha + 2.22\beta_0$
$\epsilon_3 = \alpha + 1.80\beta_0$
$\epsilon_4 = \alpha + 1.42\beta_0$
$\epsilon_5 = \alpha + 1.25\beta_0$
$\epsilon_6 = \alpha + 1.21\beta_0$
$\epsilon_7 = \alpha + 0.90\beta$
$\epsilon_8 = \alpha + 0.75\beta_0$
$\epsilon_9 = \alpha + 0.24\beta_0$
$\epsilon_{10} = \alpha - 0.05\beta_0$

DE = $6.78\beta_0$

[a] In the calculation, $\beta_{13,16}$ and $\beta_{12,17}$ of **4** as well as $\beta_{13,18}$ and $\beta_{14,17}$ of **5** were assigned the value of $0.9\beta_0$ (where β_0 represents the resonance integral of an ethylenic bond). This value ($0.9\beta_0$) appears to be more appropriate for describing the cross links, since use of $\beta_{7,10} = \beta_0$ in calculating the MO constants of **3** gave $P_{7,10} = 0.239$ which corresponds to a greatly elongated double bond.



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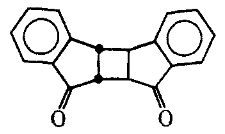

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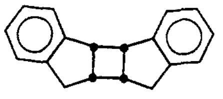

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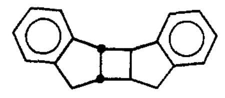

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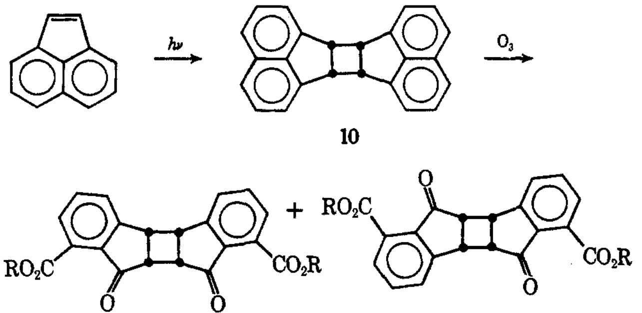

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11, R = H
13, R = CH_3

12, R = H
14, R = CH_3

Preparation of the *syn,cis* Systems 6 and 8.—*cis*-Heptacyclene (**10**), obtained by solar irradiation of a saturated solution of acenaphthylene in heptane,[22-24] was ozonized at room temperature as a suspension in 90% aqueous acetic acid. Two acidic compounds **11** and **12** were obtained in approximately equivalent amounts. These isomers could be partially separated by virtue of the difference in solubility displayed in the reaction medium. The partially separated acids were subsequently converted into their respective methyl esters **13** (mp 234–235°) and **14** (mp 179–180°), by treatment with diazomethane.

Hydrolysis of the easily purified esters **13** and **14** with concentrated hydrochloric acid afforded the pure acids **11** (mp 301–303°) and **12** (mp 291–292°). A striking feature of the spectra of these acids is the low frequency (~1630 cm^{-1}) at which the keto carbonyl groups absorb. This is to be compared with the normal frequency (~1700 cm^{-1}) which characterizes the keto carbonyl groups of **13** and **14**. This shift to lower frequencies in the case of the acids undoubtedly is due to intramolecular hydrogen bonding. This could not be confirmed through dilution studies, however, because of the low solubility of the acids in the solvents of choice.

The successful partial ozonolysis of **10** is not unexpected if one considers that ozone, acting as an electrophilic reagent, should preferentially attack the localized 1,2 bonds of the naphthalene nuclei (1.37 Å).[25] Indeed, in a kinetic investigation of the ozonolysis of naphthalene it was established that this hydrocarbon reacts rapidly with only two molecules of ozone to afford a diozonide which in turn reacts very sluggishly

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(22) K. Dziewonski and G. Rapalski, *Chem. Ber.*, **45**, 2491 (1912).

(23) K. Dziewonski and C. Paschalski, *ibid.*, **46**, 1986 (1913).

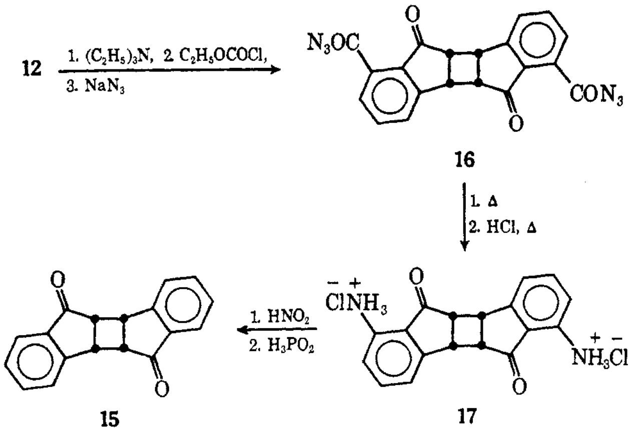
(24) For a recent discussion of the mechanism of the photodimerization of acenaphthylene, see D. O. Cowan and R. L. Drisko, *J. Amer. Chem. Soc.*, **89**, 3069 (1967).

(25) D. W. J. Cruickshank and A. P. Robertson, *Acta Crystallogr.*, **6**, 698 (1953).

with an additional three molecules of the reagent.[26]

While the gross skeletal features of the two acids **11** and **12** could be inferred from spectral and combustion analytical data, the problem of assigning the *syn* (**11**, **13**) and *anti* (**12**, **14**) configurations to the isomers remained to be solved. Preliminary insight was gained from a comparison of the nmr spectra of the isomeric esters **13** and **14**. It was observed that the two spectra differed with respect to the position of the methoxy signals. These singlets appear at τ 6.11 and 6.26 for the higher (**13**) and the lower (**14**) melting isomers, respectively. Inspection of simple models reveals that the methoxy groups of the *anti* isomer **14** unlike those of the *syn* isomer **13** lie directly opposite the aromatic nuclei. The relative upfield shift of the singlet in the spectrum of the lower melting isomer can be ascribed to a diamagnetic shielding effect experienced by the methoxy group as a result of the position, orientation, and proximity of the adjacent aromatic nucleus. On this basis the lower melting and higher melting isomers were tentatively assigned structures **14** and **13**, respectively.

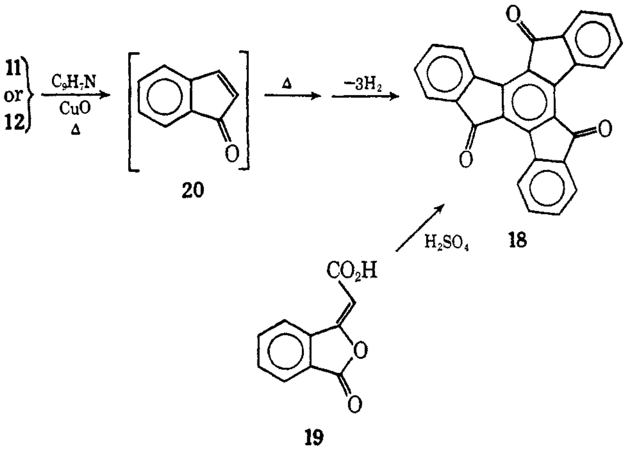
That these structural assignments are correct was ultimately verified by decarboxylation of the suspected *anti*-truxone dicarboxylic acid **12** to the known[27] *anti,-cis*-truxone **15**.



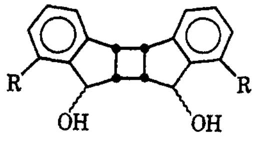
The degradation of **12** to **15** was achieved in an indirect manner which involved conversion of **12** into the bis amine hydrochloride **17** by a modified Curtius Rearrangement procedure.[28] In turn, **17** was diazotized, and the resulting bis diazonium salt converted into **15** by treatment with 30% hypophosphorous acid.

Assignment of structure **15** to the product of this degradation was made on the basis of its melting point, 191-192° (lit.[27] 194°). Furthermore, the melting point of the bisphenylhydrazone of **15** (278-280°) compares favorably with that reported for this derivative (lit.[27] 280°). That structure **15** is correct is further supported by elemental analysis and the similarity of its infrared spectrum to that of *anti,trans*-truxone (mp 293-295°).[29] This structural assignment for **12** based upon chemical evidence is in complete agreement with the tentative distinction made earlier between **13** and **14** on the basis of their respective nmr spectra.

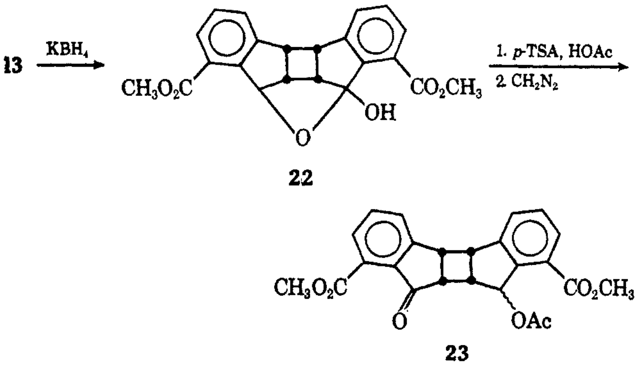
While our attempts at *direct* decarboxylation of **12** failed to give **15** the results proved interesting and provided further evidence for the gross structures of **11** and **12**. Treatment of **12**, or for that matter **11**, with cupric oxide in quinoline under reflux affords the same high melting (>360°) but readily sublimable, bright yellow solid. This substance was identified as tribenzoylenebenzene (**18**) by comparison of its infrared spectrum with that of an authentic sample prepared by treatment of phthalylacetic acid (**19**) with sulfuric acid.[30] In the formation of **18** from **11** or **12** the first step is assumed to be decarboxylation, followed by thermal cleavage to indenone (**20**), a common intermediate. Trimerization of this unstable substance[31] and subsequent aromatization would lead to the observed product **18**.



Having established the structures of **11** and **12** our efforts then turned to conversion of **13** into precursors for **4**. In an attempt to obtain the diol **21a**, the *syn* diester **13** was treated with a methanolic suspension of potassium borohydride. A product was obtained (mp 193-195°), which on the basis of spectral properties appears to be the partially reduced compound **22**.[32]



21a, R = CO_2CH_3
b, R = H



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[26] L. W. F. Kampschmidt and J. P. Wibaut, *Rec. Trav. Chim. Pays Bas*, **73**, 431 (1954); while our work was in progress R. H. Callighan, M. F. Tarker, Jr., and M. H. Wilt [*J. Org. Chem.*, **27**, 765 (1962)] reported that the ozonolysis of acenaphthene could be interrupted after destruction of only one of the two aromatic nuclei present.

[27] R. Stoermer and Fr. Moller, *Chem. Ber.*, **68**, 2124 (1935).

[28] C. Beard and A. Burger, *J. Org. Chem.*, **26**, 2335 (1961).

[29] R. Stoermer and G. Foerster, *Chem. Ber.*, **52**, 1255 (1919).

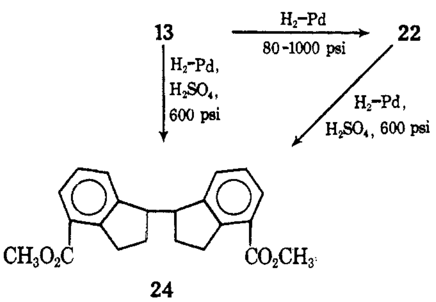
[30] R. Seka and L. Lackner, *Monatsh. Chem.*, **74**, 212 (1943).

[31] C. S. Marvel and C. W. Hinman, *J. Amer. Chem. Soc.*, **76**, 5435(1954).

[32] Related transannular participation by oxygen upon $NaBH_4$ reduction of diketones has been reported recently: P. T. Lansbury and F. D. Saeva, *ibid.*, **89**, 1890 (1967); W. C. Agosta, *ibid.*, **89**, 3505 (1967).

Treatment of the hemiketal 22 with catalytic amounts of *p*-toluenesulfonic acid in glacial acetic acid at the reflux temperature, followed by esterification with diazomethane, provided, what is presumed to be, the acetate 23 (mp 197–198°). The elemental analysis and infrared and nmr spectral data are in agreement with this assignment of structure. The carbonyl region of the spectrum is characterized by strong peaks at 1738, 1730, 1720, and 1700 cm^{-1}.

Attempts to hydrogenolyze 13 under neutral conditions proved unrewarding. It was observed that catalytic hydrogenation of 13 at room temperature over a range of pressures (80, 500, and 1000 psi) resulted in the exclusive formation of 22 rather than the desired product, namely, 7,7′-dicarbomethoxy-*syn,cis*-truxane. Hydrogenolysis of 13, as well as 22, was achieved, however, when either substrate was subjected to catalytic hydrogenation in the presence of concentrated sulfuric acid. The product isolated (mp 151–153°) in this case was assigned structure 24 on the basis of elemental analysis and the nmr data. The nmr spectrum is characterized by a multiplet at τ 2.1–3.0, a singlet at 6.15, a triplet at 7.4, a triplet at 6.85, and a multiplet centering at 7.9, in the respective area ratio of 6:6:2:4:4. The nmr data exclude the alternate isomer 25 from consideration as a possible structure for the hydrogenation product. The highest field multiplet in the spectrum of the latter should correspond to two protons in contrast to the observed four.



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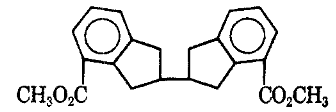

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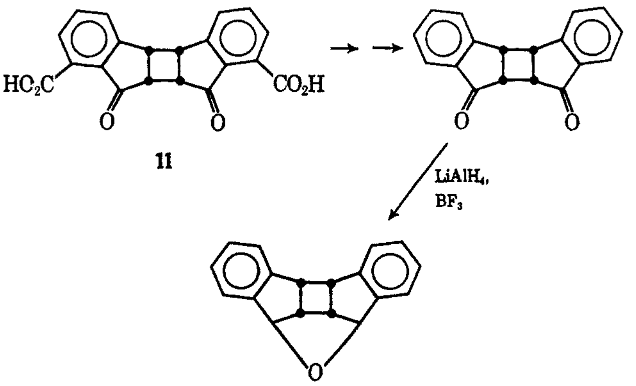
In view of the difficulties encountered in obtaining the diol 21a we focused our attention on the preparation of the unsubstituted truxane diol, namely 1,1′-dihydroxy-*syn,cis*-truxane (21b). The *syn,cis* dibasic acid 11 was thus decarboxylated, by the method described for acid 12, to yield the previously unknown *syn,cis*-truxone (6) (mp 245–247°).[33] The structure of this material was confirmed by elemental analysis and by its nmr spectrum, which shows a multiplet at τ 2.5–3.0 and two unsymmetrical triplets at 5.60 and 6.30. The symmetric disposition of the triplets about the midpoint of their separation is in agreement with the expected A_2B_2 relation between the two pairs of protons bound to the four-membered ring. Further support for structure 6 was provided by the similarity of its infrared spectrum to those of the two *anti*-truxones.

Reduction of 6 was carried out with lithium aluminum hydride in the presence of boron trifluoride ether complex, in order to circumvent the possible formation of a cyclic hemiketal.[34] The product obtained in this reduction despite the precautions taken, however, was the substituted tetrahydrofuran 26 (mp 149–151°).



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Structure 26 for the reduction product of 6 is proposed on the basis of elemental analysis and the infrared spectrum. The latter demonstrates conclusively that the molecule is devoid of hydroxyl, as well as carbonyl, functionality. Strong proof for structure 26 was obtained from the nmr spectrum which is characterized by a multiplet at τ 2.8–3.2, a quartet at 4.40, a triplet at 6.00, and a multiplet 6.40 having relative areas of 8.2:2:2:2, respectively. The most revealing aspect of this spectrum is the band at τ 4.40 due to the identically situated benzylic protons (H_a) α to the ether linkage. These protons should in theory,[35] if $J_{aa} = 0$ and $\delta_{ac} \gg J_{ac}$ (where H_c are the nonbenzylic cyclobutyl protons), give rise to three pairs of lines, each of which is symmetrically disposed about a common axis. Of these pairs, the outermost should be very weak, if observable at all, while, of the remaining two pairs, the innermost should be weaker than the central pair. These characteristics are indeed exhibited by the quartet in question. Furthermore, the triplet at τ 6.00, arising from the two *tertiary* benzylic protons (H_b), has the general features of an A_2B_2 system.

The *syn,trans* Systems.—While our work on the *syn,cis* system was in progress, the photosensitized dimerization of indene was reported.[36] The stereochemistry of the dimer, a truxane, remained to be established, however, and a study of this problem was initiated in these laboratories.

Destructive ozonolysis of indene photodimer, at room temperature, in 90% aqueous acetic acid, followed by treatment with an ethereal solution of diazomethane,

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[33] The dione 6, identical in all respects with our product, has recently been obtained by an alternate route from 5-nitroindene: C. F. Huebner, CIBA Pharmaceutical Co., Summit, N. J., personal communication.

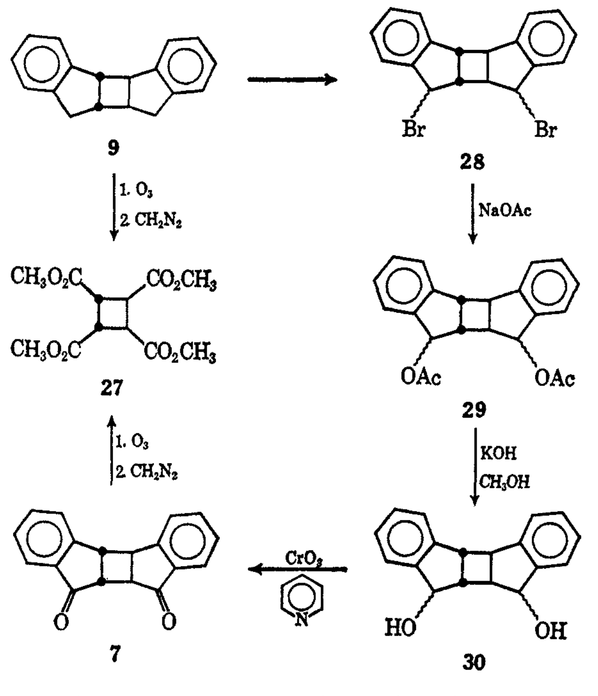
[34] This combination has been found suitable for reductions of cyclic ketals: C. H. Issidorides and A. R. Abdul-Nur, *J. Org. Chem.*, **27**, 67 (1962).

[35] 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 146.

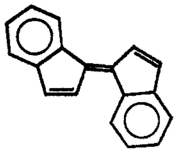
[36] Private communication from G. O. Schenck. We are indebted to Professor Schenck for making available to us the procedure as well as a generous sample of the dimer, prior to publication; see G. O. Schenck, W. Hartmann, S. Mansfield, W. Metzner, and C. H. Krauch, *Chem. Ber.*, **95**, 1642 (1962), and also C. Krauch and W. Metzner, *ibid.*, **98**, 2762 (1965), in which a preliminary report of our work is described.

provided *cis,trans,cis*-1,2,3,4-tetracarbomethoxycyclobutane (27) exclusively.[37]

These conversions, while failing to establish the entire structure of the photodimer, narrow the choices to two of the four possible truxanes, namely those possessing *trans* stereochemistry. In fact, it appeared quite probable that the dimer possessed a *syn,trans* arrangement, since the alternative *trans*-truxane, namely, *anti,-trans*-truxane (mp 116°), has been known for several decades.[38,39] Although the reported melting point of the latter hydrocarbon differed from that of **9** (mp 110–111°), we were reluctant to make an assignment in the absence of additional comparative data on derivatives of each. The "new" hydrocarbon **9** was therefore converted into the sole remaining unknown truxone, namely the *syn,trans*-truxone **7**. Toward this end the photodimer of indene was first converted into a dibromide (mp 175–177°) by treatment with 2 equiv of N-bromosuccinimide. That this dibromide possessed the expected structure **28**[40] was established by nmr spectral data. Treatment of **28** with sodium acetate in boiling glacial acetic acid led to the formation of a diacetate **29**. The structure of **29** was inferred from its infrared spectrum which showed strong peaks at 1720 and 1230 cm^{-1}. Bands in the 600 to 700 cm^{-1} region were conspicuously absent while the spectrum of **28** is characterized by strong bands in this region. The diacetate **29** was then converted into the diol **30** (mp 236–238°) by treatment with methanolic potassium hydroxide. Compound **30** shows a strong infrared band at 3220 cm^{-1} (OH), while the 1600–1800-cm^{-1} carbonyl region is devoid of any peaks. Oxidation of diol **30** was achieved with chromic anhydride in pyridine, at room temperature, and afforded as expected a truxone (mp 221–223°) differing in properties from the three previously described and on this basis assigned the remaining *syn,trans* structure **7**.[41,42] Characterization of **7** as a truxone is based upon the following data: it possesses an infrared spectrum very similar to those of the other truxones, while its melting point differs widely from those of the three known isomers; its nmr spectrum displays a multiplet at τ 2.1–2.6 and two unsymmetrical doublets at 6.95 and 6.33, in an area ratio of 8:1.9:1.9, respectively. The symmetric disposition of the doublets about the midpoint of their separation is in agreement with the A_2B_2 pattern anticipated to arise from the two nonequivalent pairs of cyclobutyl protons. Conclusive evidence that **7** incorporates a cyclobutane ring, *i.e.*, that ring opening did not occur in the conversion of **9** into **7**, was obtained on ozonolysis of **7** and subsequent esterification of the product to afford **27**.



Attempts to generate **4** from various *syn,trans*-truxane precursors to date have proved unsuccessful. However, ring opening of this truxane system has been found to yield the novel *syn*-dibenzfulvalene (**31**). We have presented details of this interesting transformation in a previous report.[43] Further work in the *syn,-trans*-truxane system will be the subject of a forthcoming report.



31

Experimental Section[44]

Partial Ozonolysis of *cis*-Heptacyclene (10).—A well-stirred suspension of **10** (13.0 g, 43 mmol) in 90% aqueous acetic acid (600 ml) was treated with a stream of ozone, at a flow rate of *ca.* 3.66 g of ozone/hr, for 8 hr at room temperature. During this period the originally white suspension turned orange, then yellow, and finally complete dissolution occurred, with the formation of a colorless solution. Oxidative decomposition of the ozonides was achieved by allowing the reaction mixture to stand in the presence of 10% hydrogen peroxide (300 ml) over a period of 48 hr. The clear solution was then refrigerated at 4° for an additional 48 hr. The resulting white precipitate, mainly **11**, was subsequently collected (5.0 g), and the filtrate left to stand at room temperature in the presence of 20% platinum-on-charcoal catalyst, for 24 hr. The catalyst was then removed by filtration and the filtrate was evaporated to dryness on a rotary evaporator to afford 7.5 g of a tan solid rich in **12**: total yield, 12.5 g (84%).

Preparation of the *syn* Ester 13.—To a well-stirred suspension of the crude acid **11** (11.0 g, 32 mmol) in benzene (250 ml), previously cooled to 5°, was added a solution of diazomethane (*ca.* 6 g) in benzene (600 ml). The resulting suspension was stirred at room temperature over a period of 20 hr. The white precipitate which was deposited (6.0 g) was then collected and proved to be essentially pure **13**, mp 229–231°. The filtrate was subsequently concentrated to approximately 30 ml to afford a nonhomogeneous precipitate consisting of large crystals of the *anti* ester **14** (700 mg), mp 179–180°, and **13** as a white powder (2.5 g), mp 225–230°. Further slow evaporation of the filtrate,

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[37] This product was not unexpected since benzylic methylene groups are readily oxidized by ozone: P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

[38] H. Stobbe and F. Zschoch, *Chem. Ber.*, **60**, 457 (1927).

[39] More recently a melting point of 143° was recorded for *anti,trans*-truxane.[40]

[40] J. Bowyer and Q. N. Porter, *Aust. J. Chem.*, **19**, 1455 (1966).

[41] N-Bromosuccinimide is known to react with benzylic methylene hydrogens in preference to methine benzylic hydrogens; see, for example, L. Horner and E. H. Winkelmann, *Angew. Chem.*, **71**, 349 (1959).

[42] The structure of the photodimer of indene was also recently elucidated by another group.[40]

[43] A. G. Anastassiou, F. L. Setliff, and G. W. Griffin, *J. Org. Chem.*, **31**, 2705 (1966).

[44] All melting points are uncorrected. Infrared spectra were determined in potassium bromide on a Perkin-Elmer Model 221 or Model 421 spectrophotometer. All nmr spectra were obtained at 60 Mc with tetramethylsilane as internal standard. Elemental analyses were performed by the Schwarzkopf Microanalytical Laboratories, Woodside 77, N. Y.

over a 2-week period, afforded an additional crop of **14** (1.2 g), which after one recrystallization from 90% aqueous methanol melted at 179–180°. The yield of **13** was 8.5 g (71.5%); that of **14** was 1.9 g (16.0%).

A single recrystallization of **13** from benzene afforded an analytical sample, mp 234–235°, in the form of strawlike white crystals. The infrared spectrum is characterized by strong bands at 1720, 1710, 1590, 1310, 1245, 1230, 1140, and 790 cm^{-1}. The nmr spectrum ($CDCl_3$) is also consistent and has peaks at τ 2.64, 5.58, 6.11, and 6.2.

Anal. Calcd for $C_{22}H_{16}O_6$: C, 70.21; H, 4.26. Found: C, 70.20, 69.92; H, 4.44, 4.27.

Proparation of the *anti* Ester 14.—The crude acid **12** was treated with diazomethane by essentially the same procedure described for the *syn* acid **11**. Filtration of the benzene suspension afforded **13** (700 mg) and an orange filtrate. The volatile solvent was subsequently removed on a rotary evaporator, and the resulting dark residue dissolved in the minimum amount of hot benzene. Upon standing at room temperature for 24 hr, the benzene solution deposited a white crystalline material (700 mg) consisting mainly of the *syn* ester **13**. The benzene mother liquor was then evaporated to dryness and the resulting residue recrystallized from methanol (Norit) to yield **14** (4.5 g) as a tan crystalline solid. The yield of **14** was 4.5 g (38%); that of **13** was 1.4 g (12%).

Successive recrystallizations of **14** from methanol yielded an analytical sample in the form of large colorless crystals, mp 179–180°. The infrared spectrum of this material is characterized by strong absorption at 1725, 1700, 1590, 1430, 1290, 1210, 1190, and 1130 cm^{-1}. The nmr spectrum ($CDCl_3$) exhibited signals at τ 2.61, 5.68, 6.2, and 6.25.

Anal. Calcd for $C_{22}H_{16}O_6$: C, 70.21; H, 4.26. Found: C, 69.90; H, 4.77.

Hydrolyses of 13 and 14 to the Pure Acids 11 and 12.—A solution of the *syn* ester **13** (100 mg, 0.27 mmol) in concentrated hydrochloric acid (20 ml) was kept at the reflux temperature over a period of 1 hr. The resulting suspension was subsequently cooled to room temperature and the precipitated solid collected, washed with water, and dried. The slightly tan crystals of **11** (80 mg, 86.6%) melted at 301–303° dec and showed the following strong infrared bands: 2635, 1725, 1712, 1630, 1580, 1475, 1432, 1300, and 755 cm^{-1}.

By the same procedure a 150-mg sample of **14** afforded 100 mg (72.5%) of acid **12**. One recrystallization from 50% aqueous acetic acid afforded pure *anti* acid (**12**), mp 291–292° dec. The infrared spectrum of this material exhibited the following strong bands: 2570, 1715, 1635, 1575, 1478, 1425, 1300, and 750 cm^{-1}.

Treatment of 11 with Quinoline and Cupric Oxide.—A suspension of the *syn* acid **11** (850 mg, 2.4 mmol) and cupric oxide (200 mg) in freshly distilled quinoline (10 ml) was kept at the reflux temperature for 3 hr. The dark reaction mixture was then cooled to room temperature and poured into ether (200 ml), and the resulting dark green precipitate collected and sublimed at 300° (0.05 mm). The bright yellow sublimate **18** had a melting point higher than 360° (lit.[36] 444°). An analytical sample of tribenzoylenebenzene having an infrared spectrum identical in all respects with that of authentic **18** (obtained from reaction of phthalylacetic acid with concentrated sulfuric acid),[30] was obtained upon treatment of the crude reaction product (300 mg) with potassium permanganate (750 mg) and sodium hydroxide (300 mg) in water (15 ml) at the reflux temperature over a period of 1 hr, followed by sublimination of the resulting brown precipitate at 300° (0.05 mm). Under similar conditions the *anti* acid **12** also afforded **18**. Tribenzoylenebenzene exhibited the following strong infrared bands: 1715, 1610, 1575, 1200, and 742 cm^{-1}.

Conversion of the *anti* Acid 12 into *anti,cis*-Truxone (15).—To a stirred suspension of **12** (950 mg, 3.0 mmol) in acetone (9 ml) and water (3 ml) maintained in an ice bath was added a solution of triethylamine (810 mg) in acetone (6 ml) followed by a solution of ethyl chloroformate (870 mg) in acetone (3 ml) and the resulting mixture was stirred at 0° for a 4-hr period. A solution of sodium azide (660 mg) in water (6 ml) was then introduced and the resulting white suspension stirred at 0° for an additional 4 hr. Water was then added, the precipitated azide (**16**) was collected and dissolved in benzene (100 ml), and the colorless benzene solution was dried over calcium sulfate.[45] The dry benzene solution was held at the reflux temperature for 24 hr. Concentrated hydrochloric acid (90 ml) was then added to this solution, and the reaction mixture was kept at a boil, with constant stirring, for an additional 24 hr. Removal of the solvents on a rotary evaporator afforded the hydrochloride **17** as a tan crystalline solid (550 mg, 55.5%). Compound **17** (500 mg) was subsequently suspended in a mixture of concentrated hydrochloric acid (15 ml) and water (15 ml) and the suspension was cooled in an ice bath. A solution of sodium nitrite (400 mg) in water (20 ml) was then added. This was followed by an excess of 30% hypophosphorous acid (150 ml), which had been precooled to 4°, and the resulting suspension held at 4°, with constant stirring over a period of 20 hr. The tan precipitate (300 mg, 84.5%) was then collected and recrystallized from methanol (Norit) to afford **15** as large colorless crystals, mp 190–192° (lit.[27] 194°). The infrared spectrum of this material is characterized by strong bands at 1700, 1600, 1470, 1285, 1050, and 760 cm^{-1}.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 83.18; H, 4.91.

The bis phenylhydrazone of this material, prepared as described,[27] melted at 278–280° dec (lit.[27] 280° dec).

Reduction of the *syn* Ester 13 with Potassium Borohydride.—An excess of potassium borohydride (240 mg) was added to a suspension of **13** (600 mg, 1.6 mmol) in methanol (60 ml) and the reaction mixture stirred at room temperature over a period of 24 hr. To the clear solution was added first glacial acetic acid (15 ml), then water (500 ml); the white precipitate (400 mg, 66%) was collected and recrystallized from 50% aqueous ethanol to afford colorless needles of **22**, mp 193–195°. The infrared spectrum of this material exhibited strong bands at 3335, 1725, 1695, 1280, and 1250 cm^{-1}. The nmr spectrum[46] ($CDCl_3$) is characterized by signals at τ 2.5–3.2 (m), 3.60 (d), 5.90 (t), 6.18 (s), and 6.45 (m) in an area ratio of 7:1:2:6:2, respectively. The presence of *one* exchangeable proton in this molecule was established upon determining the nmr spectrum in $(CF_2Cl)_2C(OD)_2$. Under these conditions the relative areas of the various signals were found to be 6:1:2:6:2, respectively.

Anal. Calcd for $C_{22}H_{18}O_6$: C, 69.83; H, 4.80. Found: C, 70.13; H, 4.79.

Treatment of 22 with *p*-Toluenesulfonic Acid.—To a solution of **22** (440 mg, 0.2 mmol) in glacial acetic acid (5 ml) were added a few crystals of *p*-toluenesulfonic acid, and the resulting mixture was kept at the reflux temperature for 6 hr. Upon standing for approximately 20 hr at room temperature, the clear solution deposited tan crystals (120 mg). To a suspension of this material (90 mg) in benzene (5 ml), kept in an ice bath, was added a solution of diazomethane (180 mg) in benzene (25 ml). The reaction mixture was then stirred overnight at room temperature. Evaporation of the volatile solvent afforded a noncrystalline solid which crystallized immediately upon trituration with absolute ethanol, 70 mg (72%). Recrystallization from ethanol afforded an analytical sample of **23**, mp 197–198°. This compound exhibited strong infrared absorption at 1738, 1730, 1720, 1700, 1300, 1265, and 1240 cm^{-1}.

Anal. Calcd for $C_{24}H_{20}O_7$: C, 68.56; H, 4.80. Found: C, 68.39; H, 5.07.

Low-Pressure Catalytic Hydrogenation of the *syn* Ester 13.—Ester **13** (200 mg, 0.53 mmol), ethyl acetate (200 ml), and 5% palladium on charcoal (180 mg) were placed in a hydrogenation flask under a pressure of 81 psi of hydrogen at room temperature. The mixture was shaken for 48 hr. The catalyst was removed by filtration, the volatile solvent evaporated, and the residual noncrystalline solid triturated with ether to afford 100 mg (50%) of a white solid. The infrared spectrum of this material proved to be identical with that of **22** (obtained from chemical reduction of **13**). Recrystallization of the crude hydrogenation product from 50% aqueous ethanol afforded colorless needles, mp 185–190°.

High-Pressure Catalytic Hydrogenation of 13.—A mixture of **13** (300 mg, 0.78 mmol), dioxane (100 ml), and 5% palladium on charcoal (150 mg) was placed in a 250-ml steel bomb at a pressure of 500 psi of hydrogen at room temperature. The mixture was shaken for 24 hr. The catalyst was removed by filtration, the filtrate was evaporated, and the residual solid was triturated with ether to yield 240 mg (80%) of **22**. The infrared spectrum

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(45) Compound **16** proved to be highly explosive as a dry solid at room temperature.

(46) Parenthesized letters refer to the splitting pattern of signals. Thus (s) = singlet, (d) = doublet, (t) = triplet, (q) = quartet, and (m) = multiplet.

was identical with that of authentic **22**. Catalytic hydrogenation of **13** under a pressure of 100 psi of hydrogen resulted in the formation of **22** in 75% yield.

High-Pressure Catalytic Hydrogenation of 13 in the Presence of Concentrated Sulfuric Acid.—Ester **13** (200 mg, 0.53 mmol), glacial acetic acid (100 ml), concentrated sulfuric acid (2 ml), and 5% palladium on charcoal (200 mg) were placed in a 250-ml steel bomb under a pressure of 600 psi of hydrogen and the mixture shaken for 36 hr. The catalyst was removed by filtration and the solvent of the filtrate evaporated at reduced pressure to afford a viscous oil. Water (60 ml) was added, the turbid aqueous solution was extracted continuously with ether for 24 hr, and the organic layer was dried over calcium sulfate. Evaporation of the volatile solvent under reduced pressure afforded a solid (160 mg, 86%), mp 138-145°. Sublimation of this material at 160° (0.05 mm) and recrystallization of the sublimate from acetone afforded an analytical sample of **24** in the form of colorless crystals, mp 151-153°. The infrared spectrum of this material showed strong bands at 1725, 1270, and 760 cm^{-1}. The nmr spectrum (CCl_4) is characterized by bands at τ 2.1-3.0 (m), 6.17 (s), 6.40 (t), 6.85, and 8.00 (m), in the respective ratio of 3:3:1:2:2.

Anal. Calcd for $C_{22}H_{22}O_4$: C, 75.41; H, 6.33. Found: C, 75.31, 75.24; H, 6.43, 6.56.

High-Pressure Catalytic Hydrogenation of 22 in the Presence of Concentrated Sulfuric Acid.—Catalytic hydrogenation of **22** was performed under the conditions described for the hydrogenation of **13**. The product (64.5%) was found to have an infrared spectrum identical with that of **24**.

Conversion of the *syn* Acid 11 into *syn,cis*-Truxone (6).—The procedure is essentially the same as described for the conversion of **12** into **15**. A 950-mg sample of **11** gave 250 mg of *syn,cis*-truxone. An analytical sample of this material was obtained after two recrystallizations from ethanol (Norit) and one from benzene: mp 245-247°. The infrared spectrum of this material is characterized by strong bands at 1700, 1600, 1285, 1275, 893, 760, 750, and 703 cm^{-1}. The nmr spectrum (CCl_4) was also consistent and showed signals at τ 2.5-3.0 (m), 5.60 (t), and 6.30 (t).

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.96; H, 4.71.

Reduction of *syn,cis*-Truxone (6) with Lithium Aluminum Hydride-Boron Trifluoride.—A suspension of lithium aluminum hydride (100 mg) in anhydrous ether (10 ml) was added over a period of 10 min to a well-stirred excess of boron trifluoride ether complex (1.4 g) kept at ice-salt temperature. A suspension of the truxone **6** (70 mg, 0.27 mmol) in anhydrous ether (5 ml) was then added, and the resulting mixture stirred, first at the ice-salt temperature for 30 min and then at the reflux temperature for 2 hr. The reaction vessel was then cooled in an ice-salt bath and 10% sulfuric acid (30 ml) was carefully added with constant stirring. The two layers were separated, the aqueous layer was extracted with ether, and the combined organic layers were washed with 10% aqueous sodium bicarbonate and dried over calcium sulfate. The volatile solvent was removed on a rotary evaporator, and the residual amorphous white solid (60 mg, 91%) recrystallized from methanol at −4°, to yield the cyclic ether **26** as colorless needles, mp 149-151° (Fisher-Jones block). The infrared spectrum of this material showed strong bands at 2930, 1029, 1015, 760, 740, and 732 cm^{-1}. The nmr spectrum exhibited signals at τ 2.8-3.2 (m), 4.40 (q), 6.00 (t), and 6.40 (m) in the respective area ratio of 4:1:1:1.

Anal. Calcd for $C_{18}H_{14}O$: C, 87.77; H, 5.73. Found: C, 87.59; H, 5.82.

Ozonolysis of Photodiindene 9.—A well-stirred suspension of **9** (2.0 g, 8.6 mmol) in 90% aqueous acetic acid (200 ml) was treated with a stream of ozone, at a flow rate of *ca.* 3.66 g of ozone/hr, for 24 hr at room temperature. Oxidative decomposition of the ozonides was achieved by allowing the clear reaction mixture to stand in the presence of 10% hydrogen peroxide (50 ml) over a period of 48 hr. The excess peroxide was subsequently destroyed with 20% platinum-on-charcoal catalyst. The catalyst was then removed by filtration and the filtrate was evaporated on a rotary evaporator to yield a viscous oil. The oil was dissolved in anhydrous ether (30 ml), excess diazomethane (approximately 4.2 g) in ether (150 ml) was added, and the reaction mixture was stirred at room temperature for 15 hr. Evaporation of the volatile solvent under reduced pressure afforded a slightly colored solid, which was recrystallized from methanol to afford 450 mg (18.2%) of colorless crystals, mp 136-142°. Two further recrystallizations of this material from methanol afforded an analytical sample with an infrared spectrum identical with that of authentic *cis,trans,cis*-tetracarbomethoxycyclobutane (**27**), mp 143-145° (lit.[47] 144-145°). Admixture of the two samples gave no melting point depression.

Anal. Calcd for $C_{12}H_{16}O_8$: C, 50.00; H, 5.60. Found: C, 50.49; H, 5.81.

Treatment of 9 with N-Bromosuccinimide. Formation of the Dibromide 28.—To a solution of **9** (10 g, 43 mmol) in dry carbon tetrachloride (150 ml) was added N-bromosuccinimide (15.4 g) and a few crystals of benzoyl peroxide, and the reaction mixture was held at reflux with constant stirring for 10 hr. The suspension was cooled to room temperature and filtered free of succinimide and the clear filtrate was evaporated on a rotary evaporator. The residual oil was subsequently digested with hot glacial acetic acid at 75° for 3 hr and the precipitated white solid (8.2 g, 49%) was collected and recrystallized from methylcyclohexane to yield 8.2 g (49%) of **28** (mp 172-175°). An analytical sample of **28** was obtained after two recrystallizations from glacial acetic acid: mp 175-178° (Fisher-Jones block). The infrared spectrum of this material exhibited strong bands at 760, 733, 680, and 630 cm^{-1}. The nmr spectrum is also consistent, with signals at τ 2.60 (s), 4.45 (s), 6.25 (d), and 7.00 (d), in a ratio of peak areas of 4:1:1:1, respectively.

Anal. Calcd for $C_{18}H_{14}Br_2$: C, 55.43; H, 3.62; Br, 40.96. Found: C, 55.38; H, 3.92; Br, 40.61.

Treatment of 28 with Sodium Acetate.—A suspension of **28** (780 mg, 2 mmol) and anhydrous sodium acetate (400 mg) in glacial acetic acid (20 ml) was kept at the reflux temperature with constant stirring over a period of 4 hr. The reaction mixture was cooled to 15°, water (150 ml) was added, and the white precipitate of **29** was collected and dried: 600 mg (86.4%). The infrared spectrum of this material showed strong bands at 1720, 1365, 1230, 1010, and 750 cm^{-1}.

Treatment of 29 with Potassium Hydroxide. Formation of the Diol 30.—A solution of **29** (500 mg, 2.0 mmol) and potassium hydroxide (10 g) in methanol (20 ml) was stirred at the reflux temperature for 24 hr. To the slightly colored reaction mixture, cooled in an ice bath, was added 6% hydrochloric acid (150 ml), followed by water (100 ml); the precipitated white solid was collected and dried: 160 mg (42.2%). An analytical sample of **30** was obtained by repeated recrystallizations from acetone: mp 236-238°. The infrared spectrum of this material exhibited strong bands at 3220, 1327, 1020, 1010, 760, and 745 cm^{-1}.

Anal. Calcd for $C_{18}H_{16}O_2$: C, 81.79; H, 6.10. Found: C, 82.44; H, 6.34.

Oxidation of 30 with Chromic Anhydride. Formation of *syn,-trans*-Truxone (7).—A suspension of **30** (200 mg, 0.8 mmol) in pyridine (3 ml) was added to a stirred slurry of chromic anhydride (1.0 g) in pyridine (10 ml). The temperature of the mixture was kept at 25° throughout the course of the addition, and the resulting dark suspension was stirred at this temperature for 15 hr. The reaction mixture was then diluted with water (100 ml) and extracted with ether. The organic layer was washed in turn with 6% hydrochloric acid, then with water, and dried over calcium sulfate. Removal of the volatile solvent afforded **7** (140 mg, 70%) as a white crystalline solid, mp 221-223°. The melting point of this material remained unchanged after recrystallization from methanol. The infrared spectrum of **7** showed strong bands at 1700, 1600, 1460, 1270, 1030, and 755 cm^{-1}. The nmr spectrum is equally consistent, τ 2.1-2.6 (m), 6.35 (d), and 6.95 (d) in the respective ratio of 4:0.96:0.96.

Anal. Calcd for $C_{18}H_{12}O_2$: C, 83.06; H, 4.65. Found: C, 82.50; H, 4.75.

Ozonolysis of *syn,trans*-Truxone (7).—A well-stirred suspension of **7** (260 mg, 1.0 mmol) in 90% aqueous acetic acid (100 ml) was treated with a stream of ozone, at a flow rate of *ca.* 3.66 g of ozone/hr, for 20 hr, at room temperature. Oxidative decomposition of the ozonides was achieved by allowing the clear reaction mixture to stand overnight in the presence of 10% hydrogen peroxide (25 ml). The excess peroxide was then destroyed with 20% platinum-on-charcoal catalyst. The catalyst was subsequently removed by filtration and the filtrate was evaporated on a rotary evaporator. The residual oil was then dissolved in anhydrous ether (15 ml), excess diazomethane (2 g) in ether (70 ml) was added, and the reaction mixture was

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(47) G. W. Griffin, J. Basinski, and A. Vellturo, *Tetrahedron Lett.*, No. 3, 13 (1960).

stirred at room temperature for 15 hr. Evaporation of the volatile solvent, under reduced pressure, afforded a white solid which was recrystallized from methanol to afford 150 mg (54.5%) of colorless crystals, mp 138–143°. The infrared spectrum of this material proved to be identical with that of authentic *cis,trans,-cis*-tetracarbomethoxycyclobutane (**27**).[47]

Registry No.—**6**, 17072-56-9; **7**, 17062-18-9; **9**, 17278-20-5; **11**, 17062-19-0; **12**, 17072-57-0; **13**, 17062-20-3; **14**, 17062-21-4; **15**, 17062-22-5; **18**, 4430-15-3; **22**, 17088-18-5; **23**, 17062-24-7; **24**, 17062-25-8; **26**, 17062-26-9; **27**, 1032-95-7; **28**, 17062-28-1; **29**, 17062-29-2; **30**, 17062-30-5.

Acknowledgment.—We are indebted to the National Science Foundation (Grants G-13759, G.P. 3764, and G.P. 2543) for financial support of this work.

Olefinic Intermediates in the Reaction of 1,1-Dimethyl-, 1,1,2-Trimethyl-, and 1,1,2,2-Tetramethylcyclopropanes with Chlorosulfonyl Isocyanate[1,2]

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1,1-Dimethylcyclopropane (**1**) on treatment with chlorosulfonyl isocyanate (CSI) led to 1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone (**2**, 73%), and, from the aqueous extract, a mixture (5%) of equal amounts of 2,3-dimethyl-3-butenamide (**3**) and 2,3-dimethyl-2-butenamide (**4**). Treatment of 2-methyl-2-butene (**5**) gave **2** (70%) and **3** (8%). Similarly, 1,1,2-trimethylcyclopropane (**6**) and CSI led to 1-chlorosulfonyl-3,3,4,4-tetramethyl-2-azetidinone (**7**, 74%) as did 2,3-dimethyl-2-butene (**8**) and CSI in 86% yield. Finally, both 1,1,2,2-tetramethylcyclopropane (**9**) and 2,3,3-trimethyl-1-butene (**12**) with CSI produced 1-chlorosulfonyl-4-*t*-butyl-4-methyl-2-azetidinone (**10**) (65 and 67%, respectively) and 3,3-dimethyl-2-methylenepentanamide (**11**) (22 and 24%, respectively). The remarkable identity of both products and yields from **1** and **5**, **6** and **8**, and **9** and **12** suggests a slow rearrangement of cyclopropanes **1**, **6**, and **9** to their respective olefins, **5**, **8**, and **12**, catalyzed by the electrophile CSI. Subsequent CSI addition to rearranged olefin leading to *β*-lactam and unsaturated amide products can be regarded as fast. The cyclopropane → olefin rearrangement pathway was confirmed by CSI addition to 1,1,2,2-tetramethylcyclopropane-3,3-d_2 (**9**-d_2) which led ultimately to **17**-d_2 and **11**-d_2 in which the deuterium present is almost exclusively in one of the methyls of the *t*-butyl group.

In preceding studies, the propensity of chlorosulfonyl isocyanate[4] (CSI) to undergo predominantly cycloaddition reactions with olefins[5,6a–c] and allenes[6d,e] has been documented. In this paper, we wish to report the reaction of CSI with the title compounds leading to the same *β*-lactam and unsaturated amide products obtained from treatment of the appropriate olefin with CSI.

Results

1,1-Dimethylcyclopropane (**1**) reacted with CSI to give 1-chlorosulfonyl-3,4,4-trimethyl-2-azetidinone (**2**, 73%), and from the aqueous extract a mixture (5%) of equal amounts[7] of 2,3-dimethyl-3-butenamide (**3**)[6d,e] and 2,3-dimethyl-2-butenamide (**4**).[6d,e,8] 2-Methyl-2-butene (**5**) and CSI gave **2** (70%) and **3** (8%). Similarly, 1,1,2-trimethylcyclopropane (**6**) and 2,3-dimethyl-2-butene (**8**) reacted with CSI to give 1-chlorosulfonyl-3,3,4,4-tetramethyl-2-azetidinone (**7**) in 74 and 86% yield, respectively. Finally, the reaction of both 1,1,2,2-tetramethylcyclopropane (**9**) and 2,3,3-trimethyl-1-butene (**12**) with CSI produced 1-chlorosulfonyl-4-*t*-butyl-4-methyl-2-azetidinone (**10**) (65 and 67%, respectively) and 4,4-dimethyl-3-methylenepentamide (**11**) (22 and 24%, respectively) (Chart I). In general, the reactions between CSI and **1**, **6**, and **9** were run at room temperature in methylene chloride solvent and required 3–48 hr for completion; olefins **5**, **8**, and **12**, however, led to products at 0° in the same solvent within 30 min.

Benzenethiol–pyridine reduction of N-chlorosulfonyl-*β*-lactams **2**, **7**, and **10** in acetone led to the appropriate unsubstituted *β*-lactams **13**, **15**, and **17**, respectively; concentrated hydrochloric acid quantitatively converted these into amino acid hydrochlorides **14**, **16**, and **18**, respectively.

Mechanism.—Currently, three mechanisms seem operative in the electrophilic, ring opening of cyclopropanes. Using **9** as an exemplary substrate with the electrophile CSI (Chart II), these include the following: (a) initial electrophilic attack followed by cleavage "between those carbons which are united with the greatest and smallest number of alkyl residues," the nucleophile "attaching itself to that carbon atom (in **19**) which carries the most alkyl radicals;"[9] (b) acid-catalyzed rearrangement of cyclopropane **9** to **12**[8b,10,11] followed by the suggested[4,5] two-step addition[12] of CSI to **12** leading to products **10** and **11** *via* the

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(2) Presented before the Organic Division, 155th National Meeting of the American Chemical Society, San Francisco, Calif., April 1968, Abstracts, p P198.

(3) (a) Taken entirely from the Ph.D. Thesis of J. F. Kelly, 1968; (b) Department of Chemistry, Massachusetts Institute of Technology, National Institutes of Health Postdoctoral Trainee, 1967–1969 (GM 015230).

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(7) Determined by vpc.

(8) (a) Undoubtedly the product of partial isomerization of **3** on long standing under acidic conditions. (b) For a quite similar $\beta,\gamma \rightleftharpoons \alpha,\beta$ equilibration of unsaturated carbonyl compounds, see R. Ya. Levina, V. N. Kostin, P. A. Gembitski, and E. G. Treschova, *J. Gen. Chem. USSR*, **30**, 883 (1960).

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