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Generation and Cycloaddition of 8,8-Dimethylisobenzofulvene[1]

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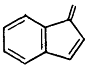
Transient 8,8-dimethylisobenzofulvene (**5**) was generated by thermal decomposition of two materials; one is formally an adduct of cyclopentadienone with 9-isopropylidenebenzonorbornadiene (**6**), and the other an adduct of 3,6-di(2′-pyridyl)-*S*-tetrazine with **6**. The former was prepared by cycloaddition of **6** to tetrachlorodimethoxycyclopentadiene followed by dechlorination giving a ketal, then hydrolysis of the ketal function. Generation without any trapping reagent instantaneously yielded one kind of dimer of a stereospecific structure. In the presence of dimethyl maleate, dimethyl 9-isopropylidenebenzonorbornene-*exo,cis*-2,3-dicarboxylate and its *endo-cis* isomer were formed. In the presence of dimethyl fumarate, the *trans* isomer was obtained. Trapping with tropone led to a 1: 1 adduct resulting from participation of the exocyclic C_2–C_8 double bond in **5**. All attempts to isolate **5** or prepare a stable metal complex of **5** by conventional means were unsuccessful.

The preparation and properties of non-planar valence bond isomers of benzene and its derivatives such as the Dewar benzenes (bicyclo[2.2.0]hexa-2,5-dienes), benzvalenes (tricyclo[3.1.0.0^{2,6}]hex-3-enes) and prismanes (tetracyclo[2.2.0.0^{2,6}.0^{3,5}]hexanes) have received considerable attention in recent years.[2–4] The planar fulvene is the most classical valence isomer and has been known for more than seventy years.[5] Benzo derivatives of these compounds can be considered as valence bond isomers of naphthalene, of which benzobenzvalene (or naphthvalene)[4] and benzofulvene (**1**)[6] are known. The isoconjugate isomer of **1**, benzoisofulvene (**2**), is of considerable interest, being isoelectronic with both the recently prepared isobenzofuran (**4a**)[7], and isobenzothiophene (**4b**)[8] known for some years. Hafner[9] was the first to succeed in the isolation of a derivative of this ring system. He isolated *N,N*-dimethyl-*N*-(1,3-diphenyl-2-indenylidenemethyl)amine (**3**) and reported on the observation of transient *N,N*-dimethyl-*N*-(2-indenylidenemethyl)amine. In connection with this, we are interested in the preparation and reactivity of 8,8-dimethylisobenzofulvene **5**.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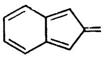
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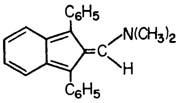

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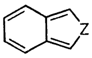

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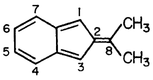
Z=O, S



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Results

The preparation of **5** was tried through two independent sequences starting from 9-isopropylidenebenzonorbornadiene (**6**), obtained by the addition of benzyne to 6,6-dimethylfulvene.[10] The first was modelled after the method of Mackenjie.[11] Heating **6** with 1,2,3,4-tetrachloro-5,5-dimethoxycyclopentadiene (**7**) at 165°C for 5 hr yielded the 1: 1 adduct (**8**)

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[1] Presented in part at the 4th Symposium on Chemistry of Nonbenzenoid Aromatic Compounds, Sendai, Japan, October 8th, 1971. Numberings used in the paper are those given in Charts.

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[3] H. R. Ward and J. S. Wishnok, *J. Amer. Chem. Soc.*, **90**, 1085 (1968); L. Kaplan and K. E. Wilzbach, *ibid.*, **90**, 3291 (1968); L. Kaplan, L. A. Wendling, K. E. Wilzbach, *ibid.*, **93**, 3821 (1971); M. G. Barlow, R. N. Haszeldine, and R. Hubbard, *J. Chem. Soc., C*, **1970**, 1232.

[4] T. J. Katz, E. J. Wang, and N. Acton, *J. Amer. Chem. Soc.*, **93**, 3782 (1971).

[5] a) J. Thiele, *Ber.*, **33**, 666 (1900); b) E. D. Bergmann, "Progress in Organic Chemistry," Vol. 3, ed. by J. W. Cook, Butterworths Publications Ltd., London, (1955), p. 81—171.

[6] R. F. C. Brown, G. E. Gream, D. E. Peters, and R. K. Solly, *Aust. J. Chem.*, **21**, 2223 (1968), and reference 25 therein.

[7] a) R. N. Warrener, *J. Amer. Chem. Soc.*, **93**, 2346 (1971); b) D. Wege, *Tetrahedron Lett.*, **1971**, 2337.

[8] R. Mayer, H. Kleinert, S. Richter, and K. Gewald, *J. Prakt. Chem.*, **20**, 244 (1963); M. P. Cava and N. M. Pollack, *J. Amer. Chem. Soc.*, **88**, 4112 (1966).

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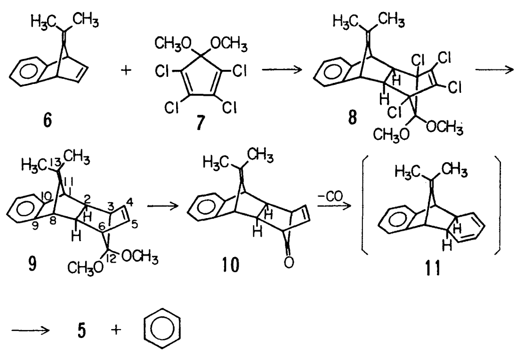
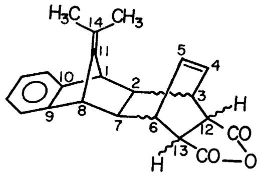
[11] a) K. Mackenjie, *J. Chem. Soc.*, **1960**, 473; K. Mackenjie and W. P. Lay, *Tetrahedron Lett.*, **1970**, 3241; W. P. Lay and K, Mackenjie, *Chem. Commun.*, **1970**, 398; b) R. McCulloch, A. R. Rye, and D. Wege, *Tetrahedron Lett.*, **1969**, 5163; c) **1969**, 5231; also Ref. 7b.



in 87% yield. Dechlorination of **8** with sodium in *t*-butyl alcohol-tetrahydrofuran gave ketal **9**, hydrolysis of which with 70% aqueous acetic acid provided ketone **10**. Stereochemistry of these compounds was determined from their PMR spectra as indicated in the chart, principally following the assignments[11b)] presented for closely related compounds; the addition compounds of norbornene or benzonorbornadiene to **7**, and their derivatives. In the stereochemistry, it is of importance that the signal assigned to H_2 (H_7) in the adduct **8** appears as a singlet at δ 2.59 ppm indicating the absence of significant spin-coupling to H_1 (H_8), and that the signal at δ 2.30 ppm due to H_2 (H_7) in the dechlorinated ketal **9** is a multiplet indicative of spin-coupling to H_3 (H_6). These observations led to the configuration in which H_2 and H_7 are *endo* to the benzonorbornene ring and *exo* to the norbornene ketal ring.

Decarbonylation of **10** in a dioxane solution proceeded at 100°C at a fair rate. Attempts to isolate the diene **11** by conventional methods were unsuccessful due to the subsequent reverse cycloaddition liberating benzene and **5**, but its formation was confirmed by the addition of maleic anhydride which rapidly forms the adduct **12**. Evidence for the indicated structure **12** was provided by the PMR spectrum (see Experimental).



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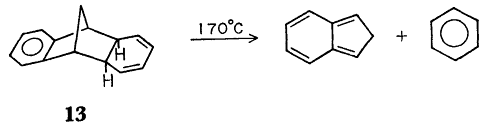

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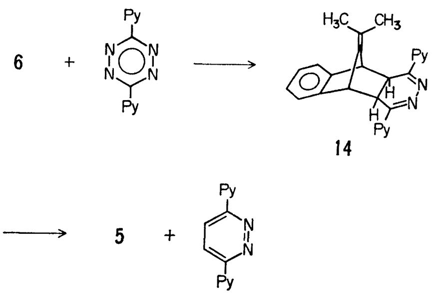
A related compound **13** prepared through the same reaction sequence starting from benzonorbornadiene instead of **6**, has been reported to require a temperature of 170°C for thermal decomposition leading to indene (presumably *via* isoindene) and benzene.[11c)] The large difference in reactivity between **11** and **13** clearly demonstrates a significant participation of the isopropylidene group in **11** in the transition state of thermal decomposition.

The second route for **5** began with the reaction of a suspension of 3,6-di(2′-pyridyl)-*S*-tetrazine[12)] with **6** in dioxane solution at room temperature (exothermic, N_2 elimination). In the dioxane solution the adduct **14** decomposed rapidly at about 50°C and slowly in the solid state on storage.



The thermal decomposition of both **10** and **14** in the absence of any trapping reagent instantaneously and quantitatively yielded only one kind of dimer (**15**, Fig. 1) displaying a remarkable stereochemical preference in dimerization. The parent peaks in the mass spectrum and elementary analysis are consistent with the formula $(C_{12}H_{14})_2$. Although the catalytic reduction of **15** resulted in no up-take of hydrogen, the Raman spectrum in chloroform revealed three kinds of unsaturated bonds at 1582(m),[13)] 1616(s), and 1708(m) cm^{-1}, assignable to unsaturation due, respectively, to a benzene ring, a cyclopentenyl double bond, and an isopropylidene double bond.[14)] The UV spectrum ($\lambda_{\max}^{\text{ether}}$ 262 mμ (ε 12810), 268 (12490), and 274 (10750)) is compatible with the existence of a double bond conjugated with a benzene ring. Confirmatory evidence for the structure was obtained by a detailed analysis of the 100 MHz PMR spectrum in $CDCl_3$. The signal assignments were made on the basis of spin-decoupling

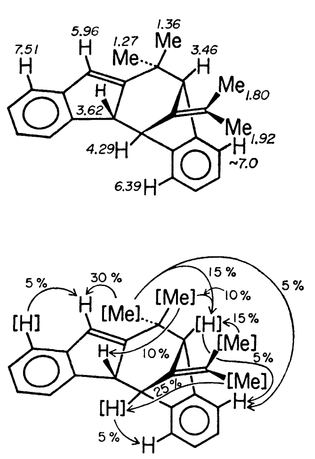


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Fig. 1. Chemical shifts (δ in ppm downfield from TMS) and nuclear Overhauser effects (indicalted by arrows) in the PMR spectrum of dimer **15** in $CDCl_3$.

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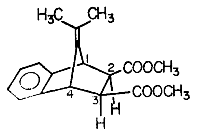
12) J. F. Geldard and F. Lions, *J. Org. Chem.*, **30**, 318 (1965),

13) m=medium, s=strong, and w=weak.

14) Raman $\nu_{C=C}$ in chloroform appear, for 7-isopropylidenebenzonorbornene,[9)] at 1725 (w) cm^{-1} (isopropylidene) and, for benzonorbornadiene, at 1620 (w) (C=C), 1607 (w) (C=C and/or benzene), and 1578 (m) (benzene). Infrared spectrum of **15** shows no absorption at 1708 cm^{-1}.

and nuclear Overhauser effect (NOE).[15,16] Chemical shifts and the positive NOE value observed are shown in Fig. 1.[17] When the signals marked by brackets were saturated with double irradiation, the positive enhancement of intensities was observed at the signals marked by arrows. It is considered that the anisotropy effect of the benzene ring of the indene moiety is responsible for the shift of the proton on the other benzene being at such a high field (δ 6.39 ppm); likewise the anisotropy effect of this latter benzene ring causes a high value for the shift of the vinyl proton (δ 5.96 ppm). Furthermore, orientation of the methine proton at position 3 of the indene moiety was established as β by the NOE results. Some coupling constants are given in Experimental. All our attempts to isolate **5** or to prepare a stable metal complex of **5** were unsuccessful. Experiments carried out are thermal decomposition of **10** and **14** under reduced pressure (1×10^{-3} mm) using a cold finger, thermal decomposition of **10** and **14** in the presence of iron pentacarbonyl, and photochemical decomposition of **10** and **14** in the absence and presence of iron pentacarbonyl. The only product characterized on these treatments was **15**.

Trapping of 5 with Dienophiles. Generation of **5** was carried out by warming dioxane solutions of **10** at 100°C (method A, Table 1) and of **14** at 50°C (method B, Table 1) in the presence of dimethyl maleate. The products were *exo-cis* adduct (**16**), *endo-cis* adduct (**17**), and dimer **15**. No detectable amount of *trans* adduct (**18**) was found by vpc. Structures of the adducts were established by their PMR spectra (Experimental). The yields of the three products varied with the amount of dimethyl maleate added (Table 1). Although the yield of **15** decreased on increasing the mole ratio of dimethyl maleate to **10** or **14**, the relative yield ratio of **16** to **17** was nearly independent of the amount of dimethyl maleate and the methods of generation. The constancy of ratio indicates the existence of an identical intermediate **5** in the decompositions of **10** and **14**. The formation of **18** but no other adduct was observed in the reaction of **10** or **14** with dimethyl fumarate.



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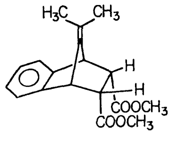

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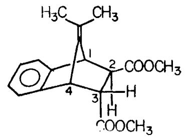

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Table 1. Products of 5 with dimethyl maleate

Method[a)]	Maleate mol ratio[b)]	Product, %[c)]			exo/endo ratio
		exo-cis **16**	*endo-cis* **17**	Dimer **15**	
A	1	10.8	5.2	42.4	2.1
	5	32.8	15.2	25.7	2.2
	10	41.9	19.8	13.9	2.1
	30	55.1	26.3	3.3	2.2
	100	56.5	26.8	0	2.1
B	30	29.1	12.3	24.1	2.4
	100	34.8	16.0	7.5	2.2

a) A: Decomposition of **10** in dioxane at 100°C. B: Decomposition of **14** in dioxane at 50°C.
b) Relative to **10** or **14**.
c) Theoretical percentage determined by vpc with an internal standard.

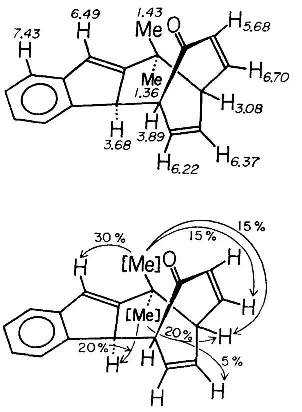
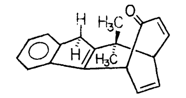


Fig. 2. Chemical shifts (δ in ppm downfield from TMS) and nuclear Overhauser effects (indicated by arrows) in the PMR spectrum of the tropone adduct **19** in $CDCl_3$.

Trapping with Tropone. Decomposition of **10** was carried out at 120°C in the presence of ten equivalents of tropone. Distillation of excess of tropone under reduced pressure left a crystalline 1 : 1 adduct in an almost quantitative yield. The IR carbonyl absorption at 1657 cm^{-1} is compatible with the presence of cyclohepta-2,5-diene but not a cyclohepta-3,5-dienone moiety. The 100-MHz PMR spectrum in $CDCl_3$ included singlet methyl signals at δ 1.36 and 1.43 ppm and five olefinic proton resonances, as well as all other signals in agreement with structure **19**, given in Fig. 2 with chemical shifts and positive NOE values observed. Appearance of the vinyl proton α to the carbonyl at such a high field as δ 5.68 ppm is thought to be due to the anisotropy effects of benzene and the ethylene bridge. Orientation of the methine proton at position 3 of the indene moiety was established as α by the NOE experiments. The proton readily underwent a base-catalyzed 1,3-shift to give **20**.



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Thus we see that **5** acts as a 6π electron addend due to participation of the exocyclic π bond in both dimerization and the tropone reaction though the mode of addition of **5** toward the 4π reactants (**5** and tropone) is just the reverse. The orbital-symmetry rule of

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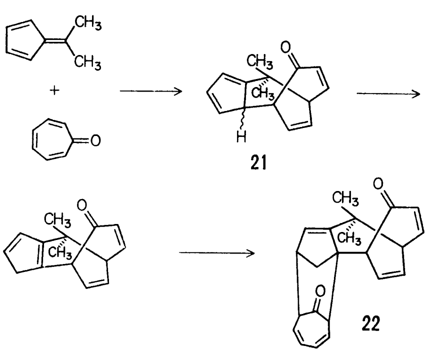
15) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **85**, 5250 (1965).

16) For experimental procedure, see K. Tori, M. Ohtsuru, I. Horibe, and K. Takeda, *Chem. Commun.*, **1968**, 943.

17) The indicated structure was consistent with the results from X-ray analysis.

Woodward and Hoffmann[18] suggests that the concerted [6+4] cycloaddition reaction has a preference for *exo* addition as far as symmetry factors are dominant. Some evidences have been reported. The tropone adduct **19** bearing the α hydrogen at position 3 might be an additional evidence, but not the dimer **15** having β hydrogen. However, the mechanism of neither reaction, whether concerted or stepwise *via* diradicals, has yet been established.

During the course of this investigation, Houk *et al.*[19] reported a cycloaddition reaction between dimethylfulvene and tropone analogous to the present reaction with tropone.[19] However, the initial adduct (**21**) is very labile because of the fact that the resulting cyclopentadiene system undergoes further addition to tropone. Thus the main product finally obtained in a stable form is a 1:2 adduct of dimethylfulvene and tropone (**22**). Their overall results are therefore very complicated. Nevertheless, their mechanistic interpretation is compatible with ours. It is suggested that the first addition of dimethylfulvene to tropone to form **21**, though not yet proven, takes place from *exo* direction.



Experimental

Melting points were taken by capillary and are corrected. Boiling points are uncorrected. Infrared spectra were determined with a Nippon Bunko IR-S spectrometer, ultraviolet spectra with a Hitachi EPS-3T spectrometer, PMR spectra with Varian A-60A and HA-100 spectrometers, and mass spectra with a Hitachi RMU-6 mass spectrometer. VPC analysis was carried out on a Hitachi gas chromatograph K-53 equipped with a hydrogen flame ionization detector and a 15 m capillary column coated with butanediol succinate or a 2 m×4 mm glass column packed with 3% diethylene glycol succinate on Chromosorb W.

Addition of 9-Isopropylidenebenzonorbornadiene (6) to 1,2,3,4-Tetrachloro-5,5-dimethoxycyclopentadiene (7). A mixture of 3.65 g (0.02 mol) of **6** and 13.2 g (0.05 mol) of **7** was heated at 165°C under nitrogen with stirring for 5 hr. After removal of excess of **7** under reduced pressure, the residue was recrystallized from pentane giving the 1:1 adduct (**8**) in 87% yield, mp 176.5—177.5°C; PMR (CCl_4) δ: ~7.00 (4, aromatic), 3.71 (s, 2, C_1,C_8–H), 3.48 (s, 6, $C\underline{H}_3O$), 2.59 (s, 2, C_2, C_7–H), and 1.65 ppm (s, 6, $C\underline{H}_3$).

Found: C, 56.80; H, 4.58; Cl, 31.72%. Calcd for $C_{21}H_{20}Cl_4O_2$: C, 56.52; H, 4.52; Cl, 31.79%.

Ketal 9 from 8. To a solution of 4.46 g (0.01 mol) of **8** in 10 m*l* of anhydrous tetrahydrofuran was added 2.76 g (0.12 g-atom) of sodium metal and 8.90 g (0.12 mol) of *t*-butyl alcohol, and the mixture was refluxed for 6 hr with stirring. After destruction of the remaining sodium by addition of methanol, the reaction mixture was concentrated by distillation of the solvent and extracted with ether. The ether solution was washed with a saturated sodium chloride solution and water, dried over sodium sulfate and evaporated. Recrystallization of the residue (2.99 g, 97% yield) from *n*-hexane yielded a pure sample of **9**, mp 155—160°C (decomp.); PMR ($CDCl_3$) δ: ~7.01 (4, aromatic), 5.88 (t, 2, $C\underline{H}$=$C\underline{H}$), 3.45 (2, s, C_1,C_8–H), 3.09 (s, 6, $C\underline{H}_3O$), 2.91 (2, m, C_3,C_6–H), 2.30 (2, qua, C_2,C_7–H), and 1.44 ppm (s, 6, $C\underline{H}_3$).

Found: C, 81.80; H, 8.01%. Calcd for $C_{21}H_{24}O_2$: C, 81.78; H, 7.84%.

Ketone 10. A suspension of 1.5 g of ketal (**9**) in 50 m*l* of 70% aqueous acetic acid was warmed at 80°C for 30 min. After dissolution of the crystals, new crystals gradually separated, which were then extracted with ether. The ether extract was washed with saturated sodium chloride solution and with water, dried and evaporated. Recrystallization of the residue (1.3 g) from a mixture of hexane and methylene chloride gave 1.07 g of **10** (83.6%), mp 140—141°C (decomp.); UV max (95% C_2H_5OH): 264 mμ (ε 1840), 270 (2700), and 276 (2810); IR (CCl_4) cm^{-1}: 1775 and 1800 (C=O); PMR ($CDCl_3$) δ: ~7.05 (4, aromatic), 6.20 (t, 2, $C\underline{H}$=$C\underline{H}$), 3.66 (2, s, C_1,C_8–H), 3.10 (qui, 2, C_3,C_6–H), 2.29 (qua, 2, C_2,C_7–H), and 1.45 (s, 6, $C\underline{H}_3$).

Found: C, 86.77; H, 6.92%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%.

Thermal Decomposition of 10 in the Presence of Maleic Anhydride. A solution of **10** (525 mg, 0.002 mol) and maleic anhydride (1.96 g, 0.02 mol) in 50 m*l* of dioxane was heated under reflux for 16 hr. Evaporation of the solvent followed by washing with ether to remove excess maleic anhydride yielded 478 mg of the adduct **12**. Recrystallization from a mixed solvent of methylene chloride and ether gave a pure sample, mp>230°C; IR ($CHCl_3$) cm^{-1}: 1756 and 1776 (acid anhydride); PMR ($CDCl_3$) δ: 6.10 (qua, 2, $C\underline{H}$=$C\underline{H}$), 3.52 (s, 2, C_1C_8–H), 3.35 (broad m, 2, C_3,C_6–H), 3.00 (t, 2, $COC\underline{H}$–$C\underline{H}CO$), 1.90 (broad s, 2, C_2,C_7–H), 1.45 (s, 6, $C\underline{H}_3$).

Found: C, 79.22; H, 6.18%. Calcd for $C_{22}H_{20}O_3$: C, 79.49; H, 6.06%.

Generation of Dimethylisobenzofulvene (5) and its Dimer (15). Method A. A solution of 510 mg of ketone **10** in 50 m*l* of dioxane was heated under reflux for 16 hr. Evaporation of the solvent yielded 333 mg of **15**, mp 155—156°C (ether-petroleum ether); mass spectrum (70 eV) *m/e* 312 (parent peak); molecular weight by osmometry 321; UV max (ether): 262 mμ (ε 12800), 268 (12500), and 274 (10800); PMR ($CDCl_3$) for δ, see Fig. 1; $J_{1.29,3.62}=3.5$ Hz[20] and positive allylic coupling $J_{3.62,5.96}$ and metabenzylic coupling $J_{7.51,3.62}$.

Found: C, 92.54; H, 8.04%. Calcd for $C_{24}H_{24}$: C, 92.26; H, 7.74%.

The decomposition of **10** was completed within 2 hr in boiling *o*-dichlorobenzene.

Method B. To a solution of 182 mg of 9-isopropylidenebenzonorbornadiene (**6**) in 5 m*l* of dioxane were added portionwise crystals of 236 mg of 3,6-di(2′-pyridyl)-*S*-tetrazine which dissolved gradually. The reaction proceeded with evolution of nitrogen to give the adduct **14**. Heating the

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[18] R. B. Woodward and R. Hoffmann, "The Conservation of Orbital Symmetry," Verlag Chemie–GmbH—Academic press. (1970), p. 145—151.

[19] K. N. Houk, L. J. Luskus, and N. S. Bhacca, *J. Amer. Chem. Soc.*, **92**, 6392 (1970); b) N. S. Bhacca, L. J. Luskus, and K. N. Houk, *Chem. Commun.*, **1971**, 109.

[20] Coupling constant, *J*, between signals at δ A and δ B is expressed as $J_{A,B}$.

dioxane solution at 50°C caused decomposition of **14**, giving **15** and 3,6-di(2′-pyridyl)pyridazine, mp 176—177°C in the absence of a trapping reagent.

Reaction of 5 with Dimethyl Maleate. Generation of **5** was conducted in the presence of dimethyl maleate by heating a dioxane solution of **10** at 100°C or one of **14** at 50°C. The results obtained are given in Table 1. The product was isolated by preparative vpc performed on a Yanagimoto gas chromatograph GCG-3 equipped with a 1 m × 14 mm stainless steel column packed with 5% diethylene glycol succinate on Chromosorb W.

The *exo-cis* adduct **16**, mp 157—158°C; UV max (95% C_2H_5OH): 262 mμ (ε 1340), 268 (2010), and 274 (2080); IR (CCl_4) cm^{-1}: 1749 (COOMe); PMR ($CDCl_3$) δ: ~7.13 (4, aromatic), 4.08 (2, s, C_1,C_4–H), 2.79 (s, 2, C_2,C_3–H), and 1.71 ppm (s, 6, $C\underline{H}_3$).

Found: C, 71.83; H, 6.56%. Calcd for $C_{18}H_{20}O_4$: C, 71.98; H, 6.71%.

The *endo-cis* adduct **17**, mp 145.5—146°C; UV max (95% C_2H_5OH): 261 mμ (ε 995), 267 (1510), and 274 (1510); IR (CCl_4) cm^{-1}: 1749 and 1731 (COOMe); PMR ($CDCl_3$) δ: 7.18 (4, aromatic), 4.05 (split t, 2, C_1,C_4–H), 3.40 (overlapped with $COOC\underline{H}_3$, 2, C_2,C_3–H), and 1.61 ppm (s, 6, $C\underline{H}_3$).

Found: C, 72.04; H, 6.76%.

The presence of dimethyl fumarate yielded the *trans* adduct **18**, mp 89—90°C; UV max (95% C_2H_5OH): 261 mμ (ε 1120), 267 (1680), and 274 (1720); IR (CCl_4) cm^{-1}: 1740 (COOMe); PMR ($CDCl_3$) δ: 7.20 (4, aromatic), 4.19 (s, 1, C_1–H), 4.15 (X part of AMX type, 1, C_4–H), 3.55 (M of AMX, 1, C_3–H), 2.95 (A of AMX (doublet), 1, C_2–H), 1.68 (s, 3, $C\underline{H}_3$), and 1.60 (s, 3, $C\underline{H}_3$).

Found: C, 72.08; H, 6.64%.

Reaction of 5 with Tropone. A mixture of 1 g (0.382 mmol) of **10** and 4.05 g (3.82 mmol) of tropone was heated at 120°C in the dark under argon atmosphere for 30 min. Removal of excess of tropone under reduced pressure left 1.02 g of crystals which were recrystallized from ether to yield a pure sample of **19**, mp 120.5—121.5°C; UV max (95% C_2H_5OH): 224 mμ (ε 21400) and 259 (11100); IR (CCl_4) cm^{-1}: 1657 (C=O); PMR ($CDCl_3$) for δ, see Fig. 2; $J_{5.68,6.70}=12.0$ Hz, $J_{6.70,3.08}=8.7$, $J_{5.68,3.08}\approx 0.2$, $J_{3.89,5.68}=1.7$, $J_{6.22,6.37}=11.5$, $J_{6.22,3.89}\approx 8$, $J_{3.08,6.37}\approx 8$, $J_{3.08,6.22}=1.7$, $J_{3.89,6.37}=1.7$, and positive allylic coupling $J_{6.49,3.68}$.

Found: C, 86.75; H, 6.89%. Calcd for $C_{19}H_{18}O$: C, 86.98; H, 6.91%.

Passing **19** through an alumina column gave the double bond isomer **20**; mp 107—108.5°C; UV max (95% C_2H_5OH): 238 mμ (ε 10100) and 261 (8950); IR (CCl_4) cm^{-1}: 1680 and 1662 (one split absorption, C=O); PMR ($CDCl_3$) δ: ~6.75 (m, 1, vinyl β to CO), ~6.2 (m, 2, $C\underline{H}$=$C\underline{H}$), 5.85 (d of d, 1, vinyl α to CO), 4.37 (d of m, 1, bridgehead α to CO in cycloheptadienone moiety), 3.37 (s, 2, benzyl), and 3.19 ppm (m, 1, bridgehead γ to CO in cycloheptadienone moiety).