

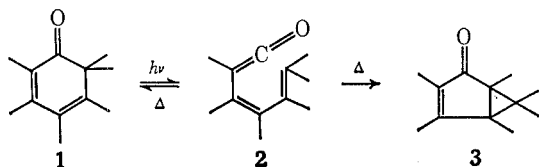
On the Mechanism of the Photoisomerization of 1(2H)-Naphthalenones¹HAROLD HART AND ROGER K. MURRAY, JR.²

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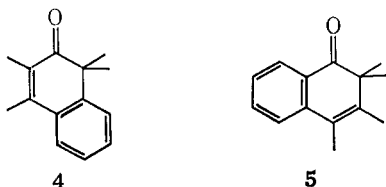
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The mechanisms operative in the photoisomerization of 2,2,3,4-tetramethyl-1(2H)-naphthalenone (5) to 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one (6) and in the subsequent photorearrangement of 6 to 2,3,4,4-tetramethyl-1(4H)-naphthalenone (7) have been investigated. Irradiation of an ether solution of 2,2,4-trimethyl-1(2H)-naphthalenone (9), prepared by the oxidation of 1,2,4-trimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate, provided 3,4,4-trimethyl-1(4H)-naphthalenone (14). This result strongly suggests that the photorearrangement of naphthalenone 5 to benzobicyclic ketone 6 proceeds by a "bond-crossing" mechanism, and does not involve alkyl migration. Photolysis of a hexane solution of naphthalenone 5 containing dimethylamine gave 6. Irradiation of a solution of 5 in methanol afforded naphthalenone 7 via 6. These results suggest that ketene 8 is not involved in the photoisomerization of 5 to 6. Irradiation of an ether solution of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone (20), prepared by the oxidation of 4-ethyl-1,2-dimethylnaphthalene with peroxytrifluoroacetic acid-boron fluoride etherate, gave 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone (22). This result strongly supports a 1,2-methyl migration mechanism for the photoisomerization of 6 to 7.

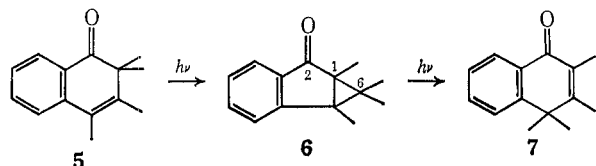
It has now been established^{3,4} that hexamethyl-2,4-cyclohexadienone (1) photoisomerizes to a ketene (2) which, in the absence of a strong nucleophile, thermally rearranges either to the starting dienone or to a bicyclo[3.1.0]hexenone (3). In order to study the influence on



the photochemistry of highly substituted 2,4-cyclohexadienones when one of the two carbon-carbon double bonds of the cyclohexadienone system belongs to a fused aromatic ring, naphthalenones 4 and 5 were synthesized.⁵ As previously reported by us,⁵ no



volatile products could be detected from the photolysis of naphthalenone 4 in ether or methanol. However, irradiation of naphthalenone 5 in ether provided benzobicyclo[3.1.0]hexenone 6 as the primary photoproduct. Further irradiation gave naphthalenone 7. In the present paper we describe an investigation of the



mechanisms for the photoisomerizations 5 → 6 and 6 → 7.

(1) We are grateful to the National Science Foundation for financial support of this research.

(2) National Institutes of Health Predoctoral Fellow, 1967-1968.

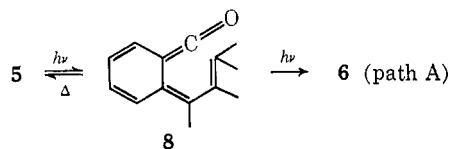
(3) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 3297 (1968).

(4) Similar observations have been made in a report concerning the photochemistry of 2,4,6-triphenyl-*o*-quinolesters: H. Perst and K. Dimroth, *Tetrahedron*, **24**, 5385 (1968). See also J. E. Baldwin and M. C. McDaniel, *J. Amer. Chem. Soc.*, **90**, 6118 (1968); M. R. Morris and A. J. Waring, *Chem. Commun.*, 526 (1969).

(5) H. Hart and R. K. Murray, Jr., *J. Org. Chem.*, **32**, 2448 (1967).

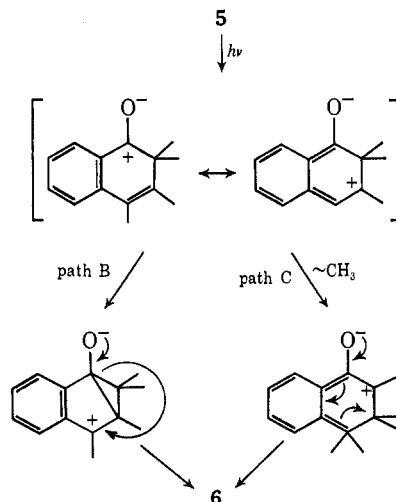
Results and Discussion

Mechanistic Considerations.—In view of previous mechanistic photochemical studies of 2,4-cyclohexadienones, three gross mechanisms can be suggested to account for the photoisomerization of 2,2,3,4-tetramethyl-1(2H)-naphthalenone (5) to 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one (6). One likely mechanism (path A) is photochemical cleavage of the 1,2 bond in naphthalenone 5 and electron reorganization to provide ketene intermediate 8. Such a ketene intermediate could thermally cyclize to the starting naphthalenone 5 or to the observed product, benzobicyclic ketone 6.³ Photochemical cleavage of the 1,6



bond in 2,4-cyclohexadienones to form *cis*-diene ketenes occurs efficiently (but not necessarily exclusively) from the n, π^* singlet state of the dienone.⁶

The photochemical conversion of 5 into 6 can also be formulated as proceeding *via* a "bond-crossing" mechanism (path B) that does not involve the intermediacy of a ketene. Ionic intermediates are used for convenience. Such a mechanism is tenable, as Griffiths and Hart⁶



(6) J. Griffiths and H. Hart, *J. Amer. Chem. Soc.*, **90**, 5296 (1968).

TABLE I
 PROPERTIES OF THE OXIDATION AND PHOTOPRODUCTS

Compd	Nmr spectra ^a		Ir spectra ^d					Elemental analysis ^f			
	Chemical shift (<i>J</i>) ^b	Assignment ^c	$\nu_{\text{C=O}}$, cm ⁻¹	$\nu_{\text{C=C}}$, conj ^d , cm ⁻¹	$\nu_{\text{C=C}}$, arom., cm ⁻¹	Uv spectra ^e		Empirical formula	C, %	H, %	
						λ , m μ	Log ϵ				
A. 1(2H)-Naphthalenones											
9	8.78 (s)	C-2 <i>gem</i> -dimethyls	1673	1635	1600	333	3.23	C ₁₃ H ₁₄ O	Calcd	83.83	7.58
	7.89 (d, 1.5)	C-4 methyl				283	3.35		Found	83.71	7.47
	4.15 (q, 1.5)	C-3 vinyl				274	3.56				
	2.30-2.70 (m)	Aromatic				266	3.54				
	1.85-2.10 (m)	Aromatic				236	4.53				
20	8.80 (s)	C-2 <i>gem</i> -dimethyls	1675	1640	1600	333	3.32	C ₁₄ H ₁₆ O	Calcd	83.95	8.05
	8.80 (t, 7.8)	Methyl (ethyl)				283	3.42		Found	83.85	8.02
	7.50 (q, 7.8)	C-4 methylene				274	3.61				
	4.25 (s, <i>W</i> _{1/2} = 3.3)	C-3 vinyl				266	3.61				
	2.55-3.13 (m)	Aromatic				236	4.74				
2.0-2.2 (m)	Aromatic										
B. 2(1H)-Naphthalenones											
13	8.62 (s)	C-1 <i>gem</i> -dimethyls	1660	1628	1604	304	4.10	C ₁₃ H ₁₄ O	Calcd	83.83	7.58
	7.68 (d, 0.9)	C-4 methyl				238	4.09		Found	83.69	7.54
	4.03 (s, <i>W</i> _{1/2} = 4.0)	C-3 vinyl				234	4.09				
	2.51-2.86 (m)	Aromatic									
24	8.69 (t, 7.8)	Methyl (ethyl)	1660	1622	1602	303	4.11	C ₁₄ H ₁₆ O	Calcd	83.95	8.05
	8.62 (s)	C-1 <i>gem</i> -dimethyls				237	4.10		Found	83.87	8.01
	7.29 (q, 7.8)	C-4 methylene				232	4.10				
	4.07 (s)	C-3 vinyl									
2.48-2.95 (m)	Aromatic										
C. 1(4H)-Naphthalenones											
7	8.52 (s)	C-4 <i>gem</i> -dimethyls	1648	1626	1605	272	4.03	C ₁₄ H ₁₆ O	Calcd	83.95	8.05
	8.02 (s, br)	C-2 methyl				256	4.06		Found	84.04	8.18
	7.93 (s, br)	C-3 methyl									
	2.57 (m)	Aromatic									
	1.9-2.1 (m)	Aromatic									
14	8.52 (s)	C-4 <i>gem</i> -dimethyls	1660	1632	1605			C ₁₄ H ₁₆ O			
	7.91 (d, 1.5)	C-3 methyl									
	3.85 (q, 1.5)	C-2 vinyl									
	2.45-2.85 (m)	Aromatic									
1.85-2.10 (m)	Aromatic										
22	9.62 (t, 7.8)	Methyl (ethyl)	1660	1631	1604	269	4.07	C ₁₄ H ₁₆ O	Calcd	83.95	8.05
	8.55 (s)	C-4 methyl				252	4.17		Found	84.02	8.09
	8.05 (q, 7.8)	C-4 methylene									
	7.94 (d, 1.5)	C-3 methyl									
	3.79 (s, <i>W</i> _{1/2} = 3.6)	C-2 vinyl									
	2.67 (m)	Aromatic									
1.93-2.12 (m)	Aromatic										

^a All spectra were determined in CCl₄. ^b Shifts are reported as τ values, with TMS as an internal reference. All spectra were run at 60 MHz. ^c All areas are consistent with the assignments. ^d All spectra are in CCl₄ and are calibrated (polystyrene). ^e All spectra are in 95% ethanol. ^f Analyses are by Spang Microanalytical Laboratories, Ann Arbor, Mich.

have found that 2,4-cyclohexadienones can be *directly* photoisomerized to bicyclo[3.1.0]hexenones *via* the first π, π^* singlet state of the dienone, if the dienone can be sufficiently perturbed by medium effects to cause inversion of the n, π^* and first π, π^* singlet states. Finally, the photoisomerization of **5** to **6** can be rationalized by a mechanism involving a 1,2-methyl migration (path C).

Whereas the primary photoproduct from the irradiation of naphthalenone **5** in ether is benzobicyclic ketone **6**, continued irradiation gave 2,3,4,4-tetramethyl-1-(4H)-naphthalenone (**7**).⁷ Naphthalenone **7**, a white solid, mp 76-78°, was shown to be isomeric with naphthalenone **5** by its elemental analysis and a parent peak at *m/e* 200 in the mass spectrum. The infrared, ultraviolet, and nmr spectra (see Table I) of **7** are all

(7) This observation was casually mentioned previously (ref 5, footnote 19), but is documented for the first time here.

consistent with the assigned structure and compare well with similar data reported for the closely related compound 3,4,4-trimethyl-1(4H)-naphthalenone (**14**).⁸ Independent irradiation of an approximately 0.5% solution of benzobicyclic ketone **6** in diethyl ether gave an 80% yield of naphthalenone **7**. Thus ketone **6** can be considered as the intermediate in the photoisomerization of **5** to **7**.

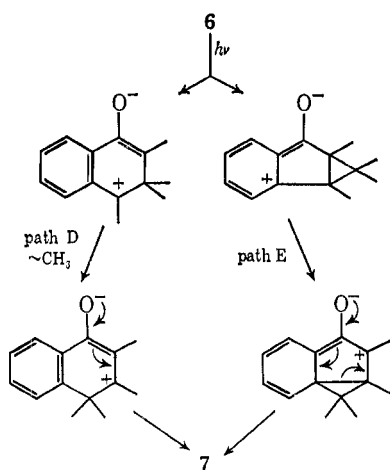
Although a few photoisomerizations of bicyclo[3.1.0]-hexenones to 2,5-cyclohexadienones are known,⁹ the reverse path is a much more common photochemical reaction.¹⁰ The reported photorearrangements of bi-

(8) J. F. Huffman and T. W. Bethea, *J. Org. Chem.*, **30**, 2956 (1965).

(9) D. H. R. Barton and W. C. Taylor, *J. Chem. Soc.*, 2500 (1958); J. Frei, C. Ganter, D. Kägi, K. Koosis, M. Miljkovic, A. Siewinski, R. Wenger, K. Schaffner, and O. Jeger, *Helv. Chim. Acta*, **49**, 1049 (1966); D. I. Schuster and A. C. Fabian, *Tetrahedron Lett.*, 4093 (1966).

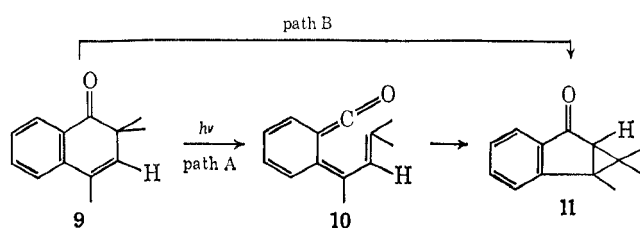
(10) For reviews see P. J. Kropp, *Org. Photochem.*, **1**, 1 (1967); K. Schaffner, *Advan. Photochem.*, **4**, 81 (1966); O. L. Chapman, *ibid.*, **1**, 323 (1963).

cyclo[3.1.0]hexenones to 2,5-cyclohexadienones usually proceed by 1,2-alkyl migration mechanisms. An analogous mechanism (path D) would account for the photoisomerization of **6** to naphthalenone **7**. The conversion of **6** into **7** can also be explained by a "bond-crossing" mechanism (path E). In such a mechanism the alkyl substituents retain their original positions.

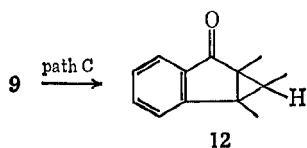


Synthesis and Photochemistry of Naphthalenone **9**.—

It appeared that paths A and B could be differentiated from path C for the photoisomerization of naphthalenone **5** to benzobicyclic ketone **6** by an examination of the photorearrangement of 2,2,4-trimethyl-1(2H)-naphthalenone (**9**). Photoisomerization of naphthalenone **9** via ketene intermediate **10** (path A) or by the "bond-crossing" mechanism (path B) would be expected to yield benzobicyclic ketone **11**. However,



photoisomerization of **9** by a mechanism that required a 1,2-methyl migration (path C) would give a different photoproduct, benzobicyclic ketone **12**.

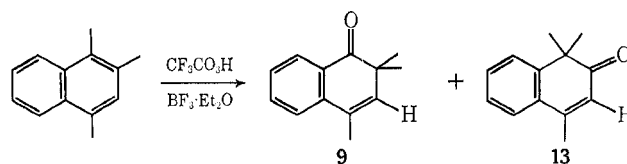


A reasonable synthesis for the desired naphthalenone **9** appeared to be the electrophilic oxidation of 1,2,4-trimethylnaphthalene. Peroxytrifluoroacetic acid-boron fluoride has been shown to be an excellent electrophilic oxidizing agent which can convert aromatic compounds directly into phenols,¹¹ alkenes into ketones,¹² and certain aromatics into 2,4-cyclohexadienones.^{5,13}

(11) C. A. Buehler and H. Hart, *J. Amer. Chem. Soc.*, **85**, 2177 (1963); H. Hart and C. A. Buehler, *J. Org. Chem.*, **29**, 2397 (1964); H. Hart, C. A. Buehler, A. J. Waring, and S. Meyerson, *ibid.*, **30**, 331 (1965).
(12) H. Hart and L. Lerner, *J. Org. Chem.*, **32**, 2669 (1967).

1,2,4-Trimethylnaphthalene was prepared *via* a modification of the method of Hewett.¹⁴ 1,2-Dimethylnaphthalene was chloromethylated with para-formaldehyde and hydrogen chloride in acetic acid. Hydrogenolysis of the resulting 1-chloromethyl-3,4-dimethylnaphthalene with lithium aluminum hydride in tetrahydrofuran provided 1,2,4-trimethylnaphthalene (Hewett used catalytic hydrogenolysis).

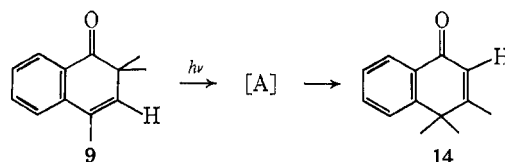
1,2,4-Trimethylnaphthalene was oxidized at -20 to -10° with a 10% excess of peroxytrifluoroacetic acid in methylene chloride. Boron fluoride etherate was added at a molar rate equal to that of the oxidant. These conditions effected an 83% conversion of 1,2,4-trimethylnaphthalene. The volatile products were separated by distillation and column chromatography and finally purified by vpc. The composition of the distillate consisted of unreacted 1,2,4-trimethylnaphthalene (42%), 2,2,4-trimethyl-1(2H)-naphthalenone (**9**, 47%), 1,1,4-trimethyl-2(1H)-naphthalenone (**13**, 9%), and an unidentified product (2%). The struc-



tures of the products follow from their analyses, spectral properties, and mode of formation. The spectroscopic and analytical data for these compounds are presented in Table I.

Naphthalenone **9** was an oil that showed conjugated carbonyl and double-bond absorptions in the infrared region and an nmr spectrum that was consistent with the assigned structure. The infrared, ultraviolet, and nmr spectra of **9** all compare well with similar data reported for the analogous naphthalenone **5**.^{5,15} Naphthalenone **13** was also an oil which had infrared, ultraviolet, and nmr spectra that compare favorably with corresponding data reported for naphthalenone **4**⁵ and 1,1-dimethyl-2(1H)-naphthalenone.¹⁶

Irradiation of a solution of naphthalenone **9** in diethyl ether through a Pyrex filter was monitored by vpc. Photolysis led to a decrease in the concentration of **9** and the appearance of a photoproduct, A, whose concentration reached a maximum of 11% of the volatiles after 3-hr irradiation and then decreased as the photolysis was continued. Another photoproduct, **14**, was also detected and the concentration of **14** continued



(13) A. J. Waring and H. Hart, *J. Amer. Chem. Soc.*, **86**, 1454 (1964); H. Hart, P. M. Collins, and A. J. Waring, *ibid.*, **88**, 1005 (1966); H. Hart and R. M. Lange, *J. Org. Chem.*, **31**, 3776 (1966); P. M. Collins and H. Hart, *J. Chem. Soc.*, 895 (1967); H. Hart and D. C. Lankin, *J. Org. Chem.*, **33**, 4398 (1968).

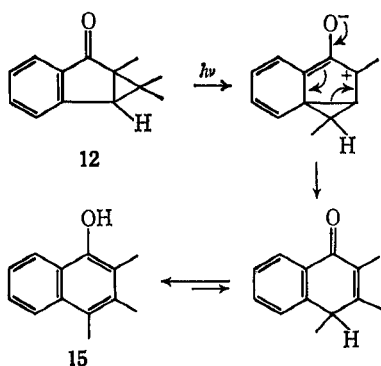
(14) C. L. Hewett, *J. Chem. Soc.*, 293 (1940).

(15) The signals at τ 8.05 and 7.90 in the reported⁵ nmr spectrum of naphthalenone **5** can now be assigned definitely to the allylic C-3 and C-4 methyls of **5**, respectively.

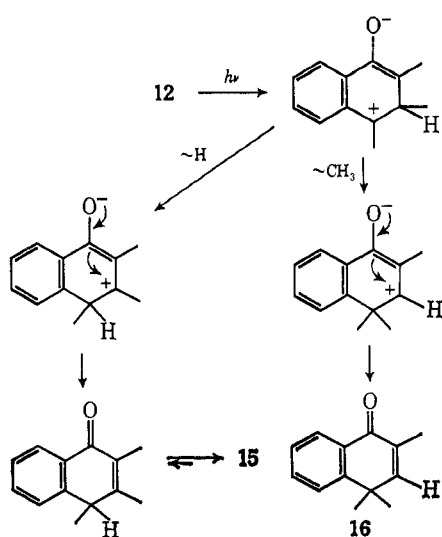
(16) N. H. Cromwell and R. C. Campbell, *J. Org. Chem.*, **22**, 520 (1957); R. C. Campbell and N. H. Cromwell, *J. Amer. Chem. Soc.*, **79**, 3456 (1957).

to increase until the photolysis was terminated. After 12-hr irradiation, vpc analysis of the photolysate indicated that the volatiles were composed of naphthalenone **9** (18%), **A** (3%), and **14** (78%). Photoproduct **14** has been identified as 3,4,4-trimethyl-1(4H)-naphthalenone. The infrared and nmr spectra of **14** are recorded in Table I. The identity of **14** was firmly established by comparison of the 2,4-dinitrophenylhydrazone derivative of the photoproduct with an authentic sample of the 2,4-dinitrophenylhydrazone of 3,3,4-trimethyl-1(4H)-naphthalenone prepared independently by Huffman and Bethea.^{8,17}

In view of the known photochemistry⁵ of 2,2,3,4-tetramethyl-1(2H)-naphthalenone (**5**), photoproduct **A** is presumed to be a benzobicyclo[3.1.0]hexenone, though it was not trapped, nor was its structure investigated. If **A** had structure **11**, then further rearrangement by mechanisms analogous to either path **D** or path **E** would lead to the observed photoproduct **14**. If **A** had structure **12**, however, then further photoisomerization to a 1(4H)-naphthalenone would be expected to provide ultimately 2,3,4-trimethyl-1-naphthol (**15**) by a "bond-crossing" mechanism analogous to path **E**, and a mixture of **15** and naphthalenone **16** via a mecha-



nism involving a 1,2-alkyl migration analogous to path **D**.

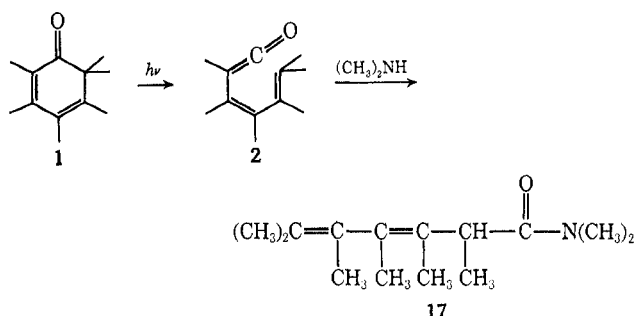


As the final photoproduct isolated in the photoisomerization of naphthalenone **9** was naphthalenone **14**, the intermediate benzobicyclohexenone (**A**) in the

(17) We thank Professor John W. Huffman of Clemson University for kindly providing a comparison sample of the 2,4-dinitrophenylhydrazone of 3,4,4-trimethyl-1(4H)-naphthalenone.

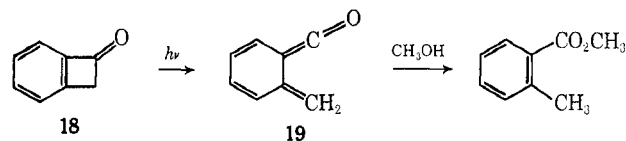
conversion of **9** into **14** must be 3,4-benzo-5,6,6-trimethylbicyclo[3.1.0]hexen-2-one (**11**). Therefore the photorearrangement of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone cannot involve methyl migration, and must occur either *via* a ketene intermediate (path **A**) or by a "bond-crossing" mechanism (path **B**). Path **C** can safely be excluded as a mechanism for the photorearrangement.

In an effort to decide between paths **A** and **B**, several attempts were made to trap the ketene **8**. The ketene intermediate **2**, formed in the photoisomerization of dienone **1** to ketone **3**, was successfully trapped by the inclusion of a strong nucleophile in the photolysis solution.⁸ Thus irradiation of **1** in alcohol or hexane with dimethylamine present provided amide **17** in high yield. However, similar irradiation of a hexane solution of tetramethylnaphthalenone **5** with an excess of



dimethylamine present was found to give only benzobicyclic ketone **6**. No other products could be detected by vpc or nmr analysis of the photolysate.

One explanation for this result is that a ketene intermediate is not involved in the photoisomerization of **5** to **6**. Contrarily, it can be contended that the reaction does proceed by a ketene intermediate, but owing to the strong driving force for rearomatization of the ketene, it thermally cyclizes to **5** or **6** faster than it reacts with an available nucleophile. However, Cava and Spangler have reported trapping a closely related ketene with a weaker nucleophile than dimethylamine.¹⁸ Thus benzocyclobutenone (**18**) is smoothly converted into methyl *o*-toluate by irradiation in methanol. The reaction is rationalized as occurring *via* ketene **19**. In a



similar experiment, irradiation of a methanol solution of naphthalenone **5** provided a high yield of naphthalenone **7** *via* the intermediate **6**. No methyl esters or other products were detected by vpc or nmr analysis of the photolysate.

Therefore it can be concluded that the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone most likely occurs by a "bond-crossing" mechanism that probably does not involve the intermediacy of a ketene. The reaction may be analogous to the direct photoisomerization of a 2,4-cyclohexadienone to a bicyclo[3.1.0]hexenone from the first π, π^* singlet state of the dienone.⁴ Alternately, if the π

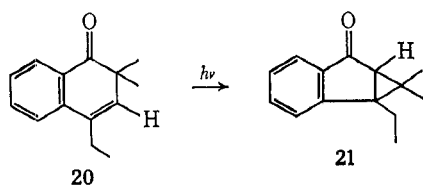
(18) M. P. Cava and R. J. Spangler, *J. Amer. Chem. Soc.*, **89**, 4551 (1967).

electrons of the aromatic ring in 1(2H)-naphthalenones do not strongly influence the photochemistry of these compounds, then the photochemistry of 1(2H)-naphthalenones can be compared with that of 3-cyclohexenones. Williams and Ziffer have shown that the characteristic photoreaction of 3-cyclohexenones in solution is isomerization to bicyclo[3.1.0]hexanones.¹⁹

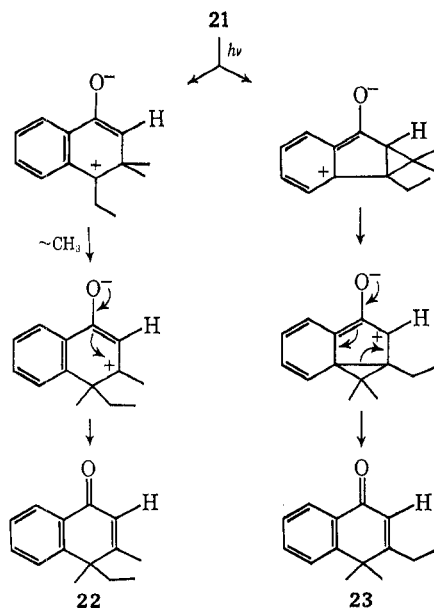
Synthesis and Photochemistry of Naphthalenone 20.

—As discussed above, the observed photochemical conversion of benzobicyclic ketone 6 into naphthalenone 7 can be formulated as proceeding by a 1,2-methyl migration (path D) or *via* a rearrangement of the “bond-crossing” type (path E). To differentiate between these alternatives, the photochemistry of 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone (20) was examined.

Since the first step in the photoisomerization of a 1(2H)-naphthalenone to a benzobicyclo[3.1.0]hexenone occurs by a “bond-crossing” mechanism, as just demonstrated, irradiation of naphthalenone 20 should provide ketone 21. Photoisomerization of 21 by a



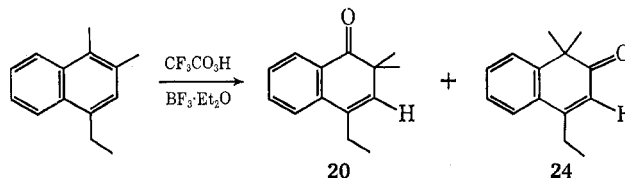
mechanism that required a 1,2-methyl migration would be expected to give naphthalenone 22. However, photorearrangement of 21 by a “bond-crossing” mechanism would be expected to yield another product, naphthalenone 23. The two ketones should be readily distinguishable by their nmr spectra. Identification of the 1(4H)-naphthalenone would permit a choice between the two mechanisms.



A suitable synthesis for the desired naphthalenone 20 appeared to be the electrophilic oxidation of 4-ethyl-1,2-dimethylnaphthalene. 1,2-Dimethylnaphthalene was acetylated with acetyl chloride–aluminum chlo-

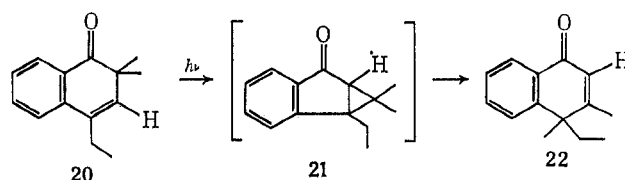
ride.²⁰ Clemmensen reduction of the resulting 1-acetyl-3,4-dimethylnaphthalene provided 4-ethyl-1,2-dimethylnaphthalene.

Oxidation of 4-ethyl-1,2-dimethylnaphthalene with peroxytrifluoroacetic acid–boron fluoride etherate at -20 to -10° effected a 78% conversion of 4-ethyl-1,2-dimethylnaphthalene. The volatile products were separated by distillation and column chromatography and finally purified by vpc. The distillate consisted of unreacted 4-ethyl-1,2-dimethylnaphthalene (41%), 4-ethyl-2,2-dimethyl-1(2H)-naphthalenone (20, 49%), and 4-ethyl-1,1-dimethyl-2(1H)-naphthalenone (24, 10%). The spectroscopic and analytical data (Table I)



for naphthalenones 20 and 24 are consistent with the assigned structures and compare very favorably with corresponding data reported for other 1(2H)⁵- and 2(1H)^{5,15}-naphthalenones, respectively.

Irradiation of a solution of naphthalenone 20 in diethyl ether through a Pyrex filter was monitored by vpc. Photolysis produced a decrease in the concentration of naphthalenone 20 and the appearance of a photoproduct whose concentration reached a maximum of 15% of the volatiles after 5-hr irradiation, then decreased as the photolysis was continued. This photoproduct is tentatively assigned the structure of 3,4-benzo-5-ethyl-6,6-dimethylbicyclo[3.1.0]hexen-2-one (21). As the irradiation was continued, another photoproduct was also detected and the concentration of this product continued to increase until the photolysis was terminated. The latter compound was isolated and has been identified as 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone (22). After 12-hr irradiation, vpc analysis



of the photolysate indicated that the volatile products were composed of 20 (30%), 21 (7%), and 22 (63%). In an attempt to increase the yield of 21, a solution of naphthalenone 20 in trifluoroethanol⁶ was irradiated through a uranium glass filter (short wavelength cut-off at *ca.* 360 m μ). Vpc analysis of the photolysis solution after brief irradiation showed that the volatile products were composed of 20 (51%), 21 (11%), and 22 (38%). Further irradiation provided an excellent yield of naphthalenone 22.

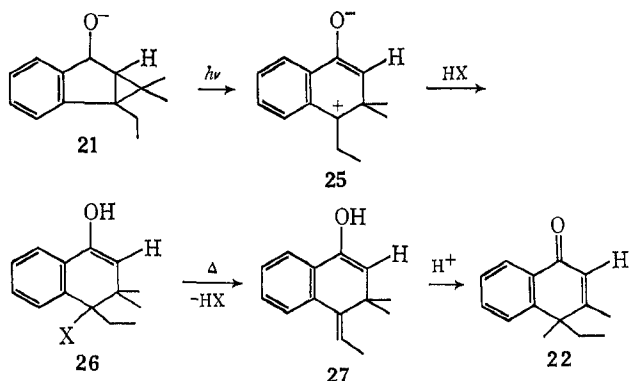
Naphthalenone 22 was an oil which showed analytical and spectroscopic data (Table I) consistent with the assigned structure. In particular, the allylic methyl (τ 7.94) of 22 is established as being at C-3, as the allylic methyl in naphthalenone 14 appears at τ 7.91, while the allylic methyls at C-2 and C-3 in naphthal-

(19) J. R. Williams and H. Ziffer, *Chem. Commun.*, 194, 489 (1967). See also K. Kojima, K. Sakai, and K. Tanabe, *Tetrahedron Lett.*, 1925 (1969).

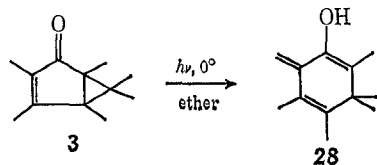
(20) P. A. Plattner and A. Ronco, *Helv. Chim. Acta*, 27, 400 (1944).

enone 7 are assigned to the signals at τ 8.02 and 7.93, respectively.²¹

Since the photoproduct isolated in the photoisomerization of naphthalenone 20 is naphthalenone 22, the photorearrangement of a benzobicyclo[3.1.0]hexenone to a 1(4H)-naphthalenone must occur *via* a 1,2-alkyl migration. Other reported photorearrangements of bicyclo[3.1.0]hexenones to 2,5-cyclohexadienones also proceed by apparent 1,2-alkyl migration mechanisms.⁹ However, the rearrangement of 20 to 22 can also be rationalized by a mechanism analogous to that elucidated by Hart and Swatton for the conversion of bicyclo[3.1.0]hexenone 3 into hexamethyl-2,5-cyclohexadienone.²² Thus the dipolar intermediate 25, photochemically generated from 21, could be trapped by a suitable nucleophile to give 26. Thermal or acid-catalyzed elimination of the nucleophile from 26 would provide the enolic triene 27, which could yield 22 on further treatment with acid.



Although Swatton²³ was able to obtain the enolic triene 28 by irradiation of a solution of bicyclo[3.1.0]hexenone 3 in anhydrous ether at 0°, no analogous



intermediates have been detected thus far in the photoisomerization of benzobicyclo[3.1.0]hexenones to 1(4H)-naphthalenones.

Experimental Section

General Photolysis Procedure.—All irradiations were conducted with a 450-W Hanovia Type L mercury arc lamp with the light filtered through a Pyrex or Corning 3320 uranium borosilicate glass sleeve. The solution to be irradiated was placed in a Pyrex test tube, sealed with a serum cap, and attached to the outside of a Hanovia water-cooled Pyrex immersion well, 2–3 cm from the center of the mercury lamp. This apparatus was then placed in a water bath, which maintained the temperature of the solution between 15 and 20° during irradiation.

For each successful irradiation experiment reported, a control experiment showed that no reaction occurred under similar conditions in the dark.

Extended Irradiation of Naphthalenone 5 in Diethyl Ether.—A solution of 115 mg of naphthalenone 5⁶ in 7 ml of diethyl ether was irradiated through a Pyrex filter. The photolysis was

monitored by vpc (10 ft \times 0.25 in. Carbowax column, 225°, 50 ml/min of helium). Aliquots examined during the first 120 min of photolysis indicated a progressive decrease in the concentration of 5 (t_R 16.6 min) and an increase in the concentration of the primary photoproduct,⁵ 3,4-benzo-1,5,6,6-tetramethylbicyclo[3.1.0]hexen-2-one (6, t_R 9.5 min). However, after 40 min of irradiation the appearance of another compound (t_R 23.6 min) was observed. After 120 min of irradiation the concentration of benzobicyclic ketone 6 decreased and the concentration of the new photoproduct sharply increased. The concentrations of 6 and the overphotoproduct were equal after 140 ± 4 min, and after 200 min of irradiation the concentration of 6 was negligible. The final photoproduct was purified by vpc (above conditions) and shown to be 2,3,4,4-tetramethyl-1(4H)-naphthalenone (7), a white solid, mp 76–78°, with spectral and analytical properties as presented in Table I.

Irradiation of Benzobicyclic Ketone 6 in Diethyl Ether.—A solution of 44 mg of benzobicyclic ketone 6⁶ in 8 ml of diethyl ether was irradiated through a Pyrex filter. Monitoring the photolysis by vpc (5 ft \times 0.25 in. DEGS 60/80 Chromosorb W column, 180°, 100 ml/min of helium) indicated the formation of a single photoproduct. This compound was purified by vpc (above conditions) and was shown to be naphthalenone 7 (see Table I for spectral properties). The photoisomerization of 6 to 7 proceeded in 80% yield.

1,2,4-Trimethylnaphthalene.—A solution of 28.0 g (0.14 mol) of 1-chloromethyl-3,4-dimethylnaphthalene¹⁴ in 200 ml of dry tetrahydrofuran was added over 1 hr to a suspension of 4.5 g (0.14 mol) of lithium aluminum hydride in 300 ml of dry, stirred, refluxing tetrahydrofuran. The mixture was stirred at reflux for an additional 24 hr and then cooled in an ice bath, and small pieces of ice were added to hydrolyze the excess lithium aluminum hydride. To this mixture was added 150 ml of 10% HCl and 150 ml of water. The resulting mixture was extracted with four 200-ml portions of ether and the separated ether layer was dried over anhydrous magnesium sulfate. Evaporation of the solvent provided 32.0 g of an oil which solidified with cooling. Recrystallization of this residue from 95% ethanol gave 12.9 g (0.076 mol) of 1,2,4-trimethylnaphthalene, yield 55%, mp 48–50° (lit.¹⁴ mp 49–50°). The ultraviolet²⁴ and nmr²⁵ spectra of 1,2,4-trimethylnaphthalene corresponded to those in the literature.

Oxidation of 1,2,4-Trimethylnaphthalene.—A solution of peroxytrifluoroacetic acid,²⁶ prepared from 0.65 ml (0.024 mol) of 90% hydrogen peroxide and 5.55 g (0.026 mol) of trifluoroacetic anhydride in 10 ml of freshly distilled methylene chloride, was cooled to -20° and added with stirring over 45 min to a solution of 3.7 g (0.022 mol) of 1,2,4-trimethylnaphthalene in 50 ml of methylene chloride which had previously been cooled to -20° . Boron trifluoride etherate (7.25 ml of 47% $BF_3 \cdot Et_2O$) was added concurrently with the addition of the peracid. The temperature of the solution was maintained between -20 and -10° throughout the addition. After further stirring for 45 min at -20° , the solution was poured into 200 ml of water and the organic layer was separated. The organic layer was washed with three 100-ml portions of water and three 150-ml portions of saturated sodium bicarbonate, extracted with three 100-ml portions of 10% aqueous sodium hydroxide, and washed with three 100-ml portions of water. The sodium hydroxide and methylene chloride fractions were investigated separately. The basic fraction was acidified with dilute hydrochloric acid and extracted with three 100-ml portions of methylene chloride, which yielded on evaporation 0.07 g of a dark, viscous oil. Vapor phase chromatography (5 ft \times 0.25 in. DEGS column, 180°, 100 ml/min of helium) indicated the presence of several components. This material was not investigated further.

The methylene chloride fraction was dried over anhydrous magnesium sulfate and evaporated to afford a deep red, viscous oil. Vacuum distillation of this material at 0.06 mm provided 1.52 g of a yellow liquid, bp 79–82°. The pot residue was 1.18 g of a deep red, very viscous material. Vapor phase chromatography (5 ft \times 0.25 in. DEGS column, 180°, 100 ml/min of helium) of the distillate showed that the crude oil had components with the following retention times: 4.6 (47%), 5.7 (42%), 6.1

(21) A methyl attached to the β carbon of a cyclic dienone exhibits a signal at lower field: P. J. Kropp, *J. Amer. Chem. Soc.*, **86**, 4053 (1964); see also ref 13.

(22) H. Hart and D. W. Swatton, *J. Amer. Chem. Soc.*, **89**, 1874 (1967).

(23) D. W. Swatton, Ph.D. Thesis, Michigan State University, 1967.

(24) E. Heilbronner, U. Fröhlicher, and P. A. Plattner, *Helv. Chim. Acta*, **32**, 2479 (1949).

(25) F. F. Yew, R. J. Kurland, and B. J. Mair, *Anal. Chem.*, **36**, 843 (1964).

(26) W. D. Emmons, *J. Amer. Chem. Soc.*, **76**, 3468 (1954).

(2%), and 9.8 min (9%). The distillate was chromatographed on silica gel in a 4 × 47 cm column. Elution with 1500 ml of pentane provided 0.64 g of 1,2,4-trimethylnaphthalene, which was identified by its melting point (49–51°), ir spectrum, and retention time (5.7 min). The conversion of 1,2,4-trimethylnaphthalene in the oxidation was 83%. Elution with 600 ml of methylene chloride provided a yellow oil which was shown to be homogeneous (t_R 4.6 min) by vpc (above conditions). Finally, elution with 350 ml of 95% ethanol provided an oil which vpc analysis indicated was composed of two compounds (t_R 6.1 and 9.8 min). Final purification of all compounds was achieved by vpc. Each compound was thermally stable under the vpc conditions. The products were identified as 2,2,4-trimethyl-1(2H)-naphthalenone (9, t_R 4.6 min) and 1,1,4-trimethyl-2(1H)-naphthalenone (13, t_R 9.8 min). Spectroscopic and analytical properties of each compound are presented in Table I and discussed in the text. An insufficient amount of the product with a retention time of 6.1 min (which composed 2% of the distillate) was obtained to permit identification.

Irradiation of Naphthalenone 9 in Diethyl Ether.—A solution of 198 mg of naphthalenone 9 in 20 ml of diethyl ether was irradiated through a Pyrex filter. Monitoring the photolysis by vpc (5 ft × 0.25 in. DEGS column, 180°, 100 ml/min of helium) showed a progressive decrease in the concentration of 9 (t_R 4.6 min) and the appearance of two new compounds with retention times of 6.0 and 18.6 min. The concentration of the compound with a retention time of 6.0 min reached a maximum of 11% of the volatiles after 3-hr irradiation and then decreased, whereas the concentration of the compound with a retention time of 18.6 min continued to increase as the photolysis was continued. After irradiation for 12 hr, vpc analysis of the photolysate indicated that the volatile products were composed of 9 (18%), a compound with a retention time of 6.0 min (3%), and a compound with a retention time of 18.6 min (78%). The photoproduct with a retention time of 18.6 min was purified by vpc (above conditions) and shown to be 3,4,4-trimethyl-1(4H)-naphthalenone⁸ (14), with spectral properties as presented in Table I. Reaction of naphthalenone 14 with 2,4-dinitrophenylhydrazine provided the 2,4-dinitrophenylhydrazone of 14, which was recrystallized from ethanol-ethyl acetate to give deep violet crystals, mp 245–247° (lit.⁸ mp 243–245°). A mixture of the 2,4-dinitrophenylhydrazone adduct of the photoproduct and an authentic sample⁷ of the 2,4-dinitrophenylhydrazone of 14 also melted at 245–247°.

Irradiation of Naphthalenone 5 in Hexane-Dimethylamine.—A solution of 114 mg (5.7×10^{-4} mol) of naphthalenone 5 and 64 mg (1.4×10^{-3} mol) of dimethylamine in 10 ml of hexane was irradiated through a Pyrex filter. The photolysis was monitored by vpc (5 ft × 0.25 in. DEGS column, 180°, 100 ml/min of helium). Examination by vpc of the photolysis solution after 30-min irradiation indicated a decrease in the concentration of naphthalenone 5 (t_R 7.0 min) and the appearance of a photoproduct with a retention time of 3.6 min. Continued irradiation caused a progressive decrease in the concentration of 5 and a corresponding increase in the concentration of the photoproduct. Vpc examination of the photolysis solution after 3-hr irradiation only showed the presence of compounds with retention times of 3.6 (45%) and 7.0 min (55%). The nmr spectrum (CCl_4) of the crude photolysate after 3-hr irradiation only had singlets at τ 9.27, 8.84, 8.73, and 8.50, in addition to the signals for unreacted naphthalenone 5. The photoproduct was purified by vpc (above conditions) and was identified by its ir spectrum (CCl_4) [1699 cm^{-1} (C=O)], nmr spectrum (CCl_4) [three-proton singlets at τ 9.27, 8.84, 8.73, and 8.50 and an aromatic multiplet centered at τ 2.60 (4 H)], and retention time as benzobicyclic ketone 6.⁵

Irradiation of Naphthalenone 5 in Methanol.—A solution of 80 mg of naphthalenone 5 in 8 ml of methanol was irradiated through a Pyrex filter. The photolysis was monitored by vpc (5 ft × 0.25 in. DEGS column, 180°, 100 ml/min of helium). Examination of the photolysis solution by vpc after 10-min irradiation showed a significant decrease in the concentration of naphthalenone 5 (t_R 7.0 min) and the appearance of a photoproduct with a retention time of 3.6 min (compound 6). After irradiation for 1 hr, analysis by vpc indicated the presence of only a single photoproduct with a retention time of 11.5 min. The nmr spectrum (CCl_4) of the crude photolysate (after irradiation for 1 hr) had a sharp singlet at τ 8.52, broad singlets at τ 8.02 and 7.92, and a complex aromatic multiplet centered at τ 2.60. The photoproduct with a retention time of 11.5 min was purified by vpc

(above conditions) and was identified by its melting point, retention time, and infrared spectrum as naphthalenone 7.

4-Ethyl-1,2-dimethylnaphthalene.—A 20.0-g sample of 1-acetyl-3,4-dimethylnaphthalene²⁰ was refluxed for 27 hr with a mixture of 70.0 g of amalgamated zinc, 70 ml of concentrated hydrochloric acid, 100 ml of methanol, and 50 ml of benzene. While the mixture was refluxing, three additional 10-ml portions of hydrochloric acid were added. The mixture was cooled and extracted with three 150-ml portions of benzene. The benzene solution was dried over anhydrous magnesium sulfate and evaporated to provide an oil. Vacuum distillation of this oil at 0.9 mm provided 11.2 g of 4-ethyl-1,2-dimethylnaphthalene, bp 130–131° [lit.²⁷ bp 136° (1 mm)]. The nmr spectrum (CCl_4) of 4-ethyl-1,2-dimethylnaphthalene consisted of a three-proton triplet ($J = 7.5$ Hz) centered at τ 8.73, three-proton singlets at τ 7.68 and 7.58, a two-proton quartet ($J = 7.5$ Hz) centered at τ 7.09, a one-proton singlet at τ 3.12, and aromatic multiplets at τ 2.75–2.92 (2 H) and 2.15–2.31 (2 H).

Oxidation of 4-Ethyl-1,2-dimethylnaphthalene.—A solution of peroxytrifluoroacetic acid,²⁸ prepared from 1.53 ml (0.055 mol) of 90% hydrogen peroxide and 12.7 g (0.06 mol) of trifluoroacetic anhydride in 20 ml of freshly distilled methylene chloride, was cooled to 0° and added with stirring over 50 min to a solution of 9.2 g (0.05 mol) of 4-ethyl-1,2-dimethylnaphthalene in 125 ml of methylene chloride which had previously been cooled to –20°. Boron trifluoride etherate (16.6 ml of 47% $BF_3 \cdot Et_2O$) was added concurrently with the addition of the peracid. The temperature of the solution was maintained between –20 and –10° throughout the addition. After further stirring for 1 hr at –20°, the solution was poured into 300 ml of water and the organic layer was separated. The organic layer was washed with two 200-ml portions of water and three 100-ml portions of saturated sodium bicarbonate, extracted with three 300-ml portions of 10% aqueous sodium hydroxide, and washed with three 300-ml portions of water.

The methylene chloride fraction was dried over anhydrous magnesium sulfate and evaporated to afford a deep red, viscous oil. Vacuum distillation of this material at 0.3 mm provided 5.1 g of yellow oil, bp 113–115°. The pot residue was 4.0 g of a black, viscous material. Vapor phase chromatography (5 ft × 0.25 in. DEGS column, 180°, 100 ml/min of helium) of the distillate showed that the crude oil had components with the following retention times: 4.1 (49%), 5.4 (41%), and 8.9 min (10%). The distillate was chromatographed on silica gel in a 4 × 45 cm column. Elution with 1000 ml of pentane provided 2.05 g of 4-ethyl-1,2-dimethylnaphthalene, which was identified by its ir spectrum and retention time (5.4 min). The conversion of 4-ethyl-1,2-dimethylnaphthalene in the oxidation was 78%. Elution with 600 ml of methylene chloride provided an oil which vpc analysis (above conditions) showed had two components with retention times of 4.1 (90%) and 8.9 min (10%). Finally, elution with 500 ml of a 1:1 mixture of methylene chloride–95% ethanol afforded an oil which was shown to be homogeneous (t_R 8.9 min) by vpc (above conditions). Final purification of all compounds was achieved by vpc. Each compound was thermally stable under the vpc conditions. In order of increasing retention times, the products were identified as 4-ethyl-2,2-dimethyl-1-(2H)-naphthalenone (20) and 4-ethyl-1,1-dimethyl-2(1H)-naphthalenone (24). Spectroscopic and analytical properties of each compound are presented in Table I and discussed in the text.

Irradiation of Naphthalenone 20 in Diethyl Ether.—A solution of 167 mg of naphthalenone 20 in 17 ml of diethyl ether was irradiated through a Pyrex filter. Monitoring the photolysis by vpc (5 ft × 0.25 in. DEGS column, 180°, 100 ml/min of helium) showed a progressive decrease in the concentration of naphthalenone 20 (t_R 4.2 min) and the appearance of two new compounds with retention times of 5.4 and 15.5 min. The concentration of the compound with a retention time of 5.4 min reached a maximum of 15% of the volatiles after 5-hr irradiation and then decreased, whereas the concentration of the compound with a retention time of 15.5 min continued to increase as the photolysis was continued. After irradiation for 16 hr, vpc analysis of the photolysate indicated that the volatiles were composed of 20 (30%), a compound with a retention time of 5.4 min (7%), and a compound with a retention time of 15.5 min (63%). The photoproduct with a retention time of 15.5 min was purified by

(27) W. Cocker, L. O. Hopkins, L. Mabrouk, J. McCormick, and T. B. H. McMurry, *J. Chem. Soc.*, 2230 (1960).

vpc (above conditions) and was identified as 4-ethyl-3,4-dimethyl-1(4H)-naphthalenone (22). The spectroscopic properties of naphthalenone 22 are presented in Table I.

Irradiation of Naphthalenone 20 in Trifluoroethanol.—A solution of 50 mg of naphthalenone 20 in 5 ml of trifluoroethanol was irradiated through a uranium glass filter (short wavelength cut-off at ca. 360 m μ). Vapor phase chromatography (5 ft \times 0.25 in. DEGS column, 180°, 100 ml/min of helium) of the photolysis solution after 15-min irradiation showed that the photolysate had components with the following retention times: 4.1 (naphthalenone 20, 51%), 5.4 (11%), and 15.3 min (38%). Examination of the photolysate by vpc after irradiation for 1 hr indicated the

presence of a single component with a retention time of 15.3 min. The photoproduct was purified by vpc and was identified by its infrared spectrum and retention time as naphthalenone 22.

Similarly, irradiation of a solution of 110 mg of naphthalenone 20 in 11 ml of trifluoroethanol through a Pyrex filter for 2 hr proceeded with complete conversion and provided a 90% yield of naphthalenone 22.

Registry No.—7, 23740-88-7; 9, 23740-89-8; 13, 23740-90-1; 14, 2981-97-7; 20, 23740-92-3; 22, 23740-93-4; 24, 23740-94-5.

Titanium Tetrachloride Promoted Condensations of Amines with Carboxamides and Similar Species

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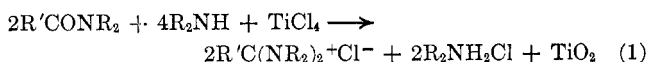
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Titanium tetrachloride-amine complexes aminate nonhindered carboxamides, β -dicarbonyl compounds, and vinylogous carboxylic acids. Amidinium and vinylogous amidinium salts are formed. In the presence of excess amine, certain amidinium ions are converted into their conjugate bases, enediamines.

Recently we have reported the titanium tetrachloride promoted amination of carbonyl compounds to give enamines,^{1a} imines,^{1b} and carboxamides.² We report here the further amination of carboxamides, which give amidinium salts,³ and the amination of β diketones and tropolone, which can be regarded as vinylogous carboxylic acids and which give vinylogous amidinium salts as products. This reaction provides a very convenient route to symmetrically substituted amidinium salts and their derivatives.

Results and Discussion

Amination reactions were carried out on a number of representative carboxamides, acetylacetone, and tropolone, the results of which are collected in Table I. Dimethylamine was generally used as the amine component of the reagent to simplify nmr spectral analysis of the products, but other amines, e.g., N,N'-dimethylethylenediamine and 1,2-dimethylhydrazine, proved equally effective. The reaction follows the stoichiometry of eq 1. The reactions were run in a solvent;



THF or excess dimethylamine (under pressure) proved particularly convenient.

The amination of carboxamides is a significantly more difficult reaction to accomplish than the amination of ketones or carboxylic acids. While virtually any ketone can be converted into its corresponding enamine and any carboxylic acid into its amide by the complexes formed in the interaction of TiCl₄ with primary or secondary amines,⁴ only nonsterically hindered amides undergo further amination. Thus the N,N-dimethyl-

amides of formic, acetic, and propionic acids react (with decreasing rapidity) with the TiCl₄-(CH₃)₂NH reagent to give good yields of tetramethylamidinium salts, but with the more highly substituted isobutyric amide the reaction stops at an intermediate stage, and N,N-dimethylpivalamide is inert. On the other hand, N,N-dimethyldichloroacetamide and N,N-dimethylphenylacetamide react fairly readily, showing that there is a delicate balance among factors which determine the reactivity of these compounds.

Tropolone is about as reactive as carboxylic acids toward amination, but acetylacetone reacts very rapidly to give a high yield of vinylogous amidinium salt product.

The product isolated from each reaction is apparently dependent on the acidity of the initially formed amidinium ion. In general, compounds without a hydrogen atom α to the carboxyl group, alkyl derivatives of acetic acid, acetylacetone, and tropolone yield the amidinium (or vinylogous amidinium) salt, whereas electronegatively substituted acetic acids yield enediamines. With dimethylacetamide itself, the reaction can be run so as to yield either tetramethylacetamidinium chloride (1) or its conjugate base, vinylidenebis(dimethylamine) (2).⁵ Evidently, the α -hydrogen-bearing amidinium ions are carbon acids of the same order of acid strength as dimethylammonium ion, and in the presence of excess dimethylamine (as these reactions are normally run) the stronger acids are converted into their conjugate bases.

However, N,N,N',N'-tetramethylpropanamidinium chloride (3) is not so converted into its conjugate base, which implies that it must be a considerably weaker acid than 1.⁶ This is not the anticipated

(1) (a) W. A. White and H. Weingarten, *J. Org. Chem.*, **32**, 213 (1967).
(b) H. Weingarten, J. P. Chupp, and W. A. White, *ibid.*, 3246 (1967).

(2) J. D. Wilson and H. Weingarten, *Can. J. Chem.*, **48**, 983 (1970).

(3) After this work was completed, a brief report of the preparation of some complex cyclic amidinium ions by a similar procedure was published: R. Ian Fryer, J. V. Earley, G. F. Field, W. Zally, and L. H. Stembach, *J. Org. Chem.*, **34**, 1143 (1969).

(4) R. T. Cowdell and G. W. A. Fowles, *J. Chem. Soc.*, 2522 (1960).

(5) H. Weingarten and W. A. White, *J. Amer. Chem. Soc.*, **88**, 850 (1966); *J. Org. Chem.*, **31**, 2874 (1966).

(6) This was verified experimentally by observing the nmr spectra of mixtures of 1 with the conjugate base of 3, propenylidenebis(dimethylamine), and of 3 with vinylidenebis(dimethylamine). The equilibrium mixture was found to consist almost entirely of 3 and vinylidenebis(dimethylamine), the other two components being undetectable by nmr; thus 3 is at least one order of magnitude weaker an acid than 1.