

etheral layer was washed (water) and dried (magnesium sulfate). Distillation gave the dioxolane, b.p. 76–78° (20 mm.),  $n_D^{20}$  1.4307 [lit.<sup>17</sup> b.p. 87° (22 mm.),  $n_D^{18}$  1.4326],  $\nu_{\max}$  1640 (w) (–C=C–) and 926  $\text{cm}^{-1}$  (–CH=CH<sub>2</sub>).

**Rearrangement of 2,2-Dimethyl-4-(allyloxymethyl)dioxolane.**—A mixture of 0.3 ml. of the dioxolane Xa and 117 mg. of potassium *t*-butoxide in 4 ml. of dry dimethyl sulfoxide was left at room temperature for 3 days. The mixture was poured into water and extracted with ether, and the etheral extracts were washed with water and dried over anhydrous magnesium sulfate. Evaporation gave 2,2-dimethyl-4-(prop-1'-enyloxymethyl)dioxolane (XIa) as an oil showing infrared absorption bands at 1666 (s) (*cis* O=C=C–) and 723  $\text{cm}^{-1}$  (*cis* CH=CH), and no absorption at 1640 or 926  $\text{cm}^{-1}$ .

**2,2-Dimethyl-4-(2'-butenyloxymethyl)dioxolane (Xb).**—Pre-

pared in the same manner as Xa using 6.8 g. of 1-bromo-2-butene, the dioxolane was obtained (5 g., 53% yield) as an oil, b.p. 95° (20 mm.),  $n_D^{20}$  1.4362, showing infrared absorption bands at 1660 (w) and 967  $\text{cm}^{-1}$  (*trans* CH=CH bending).

The compound was recovered unchanged after attempted rearrangement with potassium *t*-butoxide in dimethyl sulfoxide.

**Acknowledgment.**—We wish to thank Dr. W. E. M. Lands for a sample of the 1-alkenylacylglycerol isolated from natural pig heart plasmalogen and are grateful to Dr. R. Aplin for obtaining the mass spectra and for helpful discussion and to Dr. N. S. Bhacca for the 100-Mc. n.m.r. spectrum.

## Ketenes. V. Reactions of Ketenes with Dienes and Olefins<sup>1</sup>

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Butylethylketene undergoes 1,2 cycloadditions with 1,3-butadiene, alkyl-substituted butadienes, and 1,3-butadienyl methyl ether to give substituted cyclobutanones. Methyl 1-methylenallyl ether combines with ketenes in a 1,4 addition to give 5,6-dihydro-4-methoxy-2H-pyrans. Cyclopentadiene and indene add 1,2 to dimethylketene. 2,4-Dimethyl-2,3-pentadiene reacts very readily with ketenes to give cyclobutanones. Butylethylketene undergoes 1,2 cycloadditions with nonactivated cyclic and acyclic olefins at elevated temperatures to give cyclobutanones.

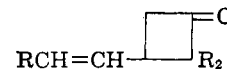
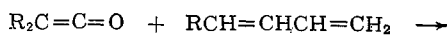
Ketenes usually add to monoolefinic compounds by 1,2 cycloaddition. Where the evidence is well documented, the tendency for 1,2 cycloaddition also applies in the reaction of ketenes with conjugated dienes. Staudinger and Suter noted the ready reaction of diphenylketene with isoprene and with 2,3-dimethyl-1,3-butadiene, but they isolated no crystalline products, and only surmised that 1,4 cycloaddition took place to form cyclohexenones.<sup>2</sup> Later studies showed, through definite structural assignments, that diphenylketene formed 1,2 cycloadducts with cyclic dienes<sup>3–8</sup>; by analogy, and with good evidence against 1,4 cycloaddition, the reaction with acyclic dienes was formulated in the same way.<sup>3,5,9</sup>

Similar studies with ketene and the higher aliphatic ketenes have been limited chiefly to adducts with cyclopentadiene,<sup>10–19</sup> and here 1,2 cycloaddition is also firmly established. A low yield of 1,2-cycloadduct was obtained from the reaction of 1,3-butadiene with ketene.<sup>20</sup> Isoprene<sup>21</sup> and 2,3-dimethyl-1,3-butadiene<sup>22</sup>

did not react with ketene at low to moderate temperatures, but at 600° some 1,4 cycloaddition to the latter diene was suggested.<sup>22</sup> Only one addition of higher aliphatic ketenes to acyclic dienes has been reported.<sup>23</sup> Bestian and Günther generated dimethylketene at 140° in the presence of excess 1,3-butadiene to give a 1,2-cycloadduct.

After a thorough consideration of prior work in the field, the following generalizations can be made: (1) diphenylketene is very reactive with dienes even at room temperature; (2) dimethylketene is less reactive than diphenylketene and dimerizes rapidly, so that cycloadditions are possible only at moderate temperatures and with fairly nucleophilic olefins (except when the dimethylketene is generated *in situ* at elevated temperatures in the presence of a diene); (3) butylethylketene is less reactive than dimethylketene, but because of its slow rate of dimerization, cycloadditions have been forced with various olefins by use of higher temperatures<sup>24</sup>; and (4) ketene is even less reactive than butylethylketene in 1,2 cycloaddition reactions and generally must be heated, even with such active dienes as cyclopentadiene.

This paper describes our work concerning the cycloaddition of a variety of dienes to ketenes. We observed that dialkylketenes undergo 1,2 cycloaddition with dienes to give 3-vinylcyclobutanones, according to the general equation



(21) C. D. Hurd, A. D. Sweet, and C. L. Thomas, *J. Am. Chem. Soc.* **55**, 335 (1933).

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(1) Paper IV: R. H. Hasek, P. G. Gott, and J. C. Martin, *J. Org. Chem.*, **29**, 2513 (1964).

(2) H. Staudinger and E. Suter, *Ber.*, **53**, 1092 (1920).

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(6) J. R. Lewis, G. R. Ramage, J. L. Simonsen, and W. G. Wainwright, *J. Chem. Soc.*, 1837 (1937).

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(15) H. A. Berson and J. W. Patton, *ibid.*, **84**, 3406 (1962).

(16) J. M. Witzel, Ph.D. Thesis, Cornell University, 1941.

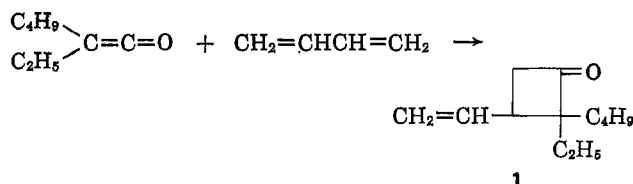
(17) M. D. Owen, *J. Indian Chem. Soc.*, **20**, 343 (1943).

(18) W. Rellensmann and K. Hafner, *Chem. Ber.*, **95**, 2579 (1962).

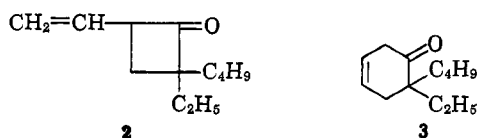
(19) H. Staudinger and P. J. Meyer, *Helv. Chim. Acta*, **7**, 19 (1924).

(20) E. Vogel and K. Müller, *Ann. Chem.*, **615**, 29 (1958).

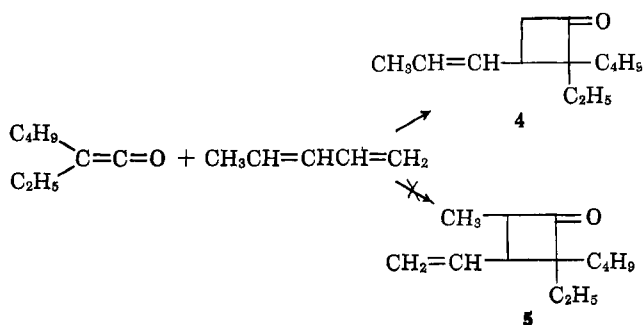
Butylethylketene reacted with 1,3-butadiene at 150° to give 2-butyl-2-ethyl-3-vinylcyclobutanone (1) in 45% yield. The structure of 1 was proved by a combi-



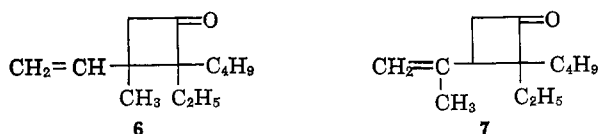
nation of elemental analysis and infrared and n.m.r. spectra. Infrared bands at 5.62  $\mu$ <sup>25</sup> showed that the adduct was a cyclobutanone, and bands at 6.12 and 9.98  $\mu$  demonstrated the presence of a terminal vinyl group. The n.m.r. spectrum<sup>26</sup> verified the presence of a terminal vinyl group and showed a methylene group adjacent to a carbonyl group. The methylene groups adjacent to the carbonyl group in cyclobutanone occur at 3.03 p.p.m., while the remaining methylene group occurs at 1.96 p.p.m.<sup>27</sup> The methylene group in 1 was at 2.90 p.p.m. These data rule out the alternate structures 2 and 3. Butylethylketene and 1,3-penta-



diene, heated at 180°, gave 2-butyl-2-ethyl-3-propenylcyclobutanone (4) in 64% yield and *not* the alternate structure 5. In the gas-liquid partition chromatogram

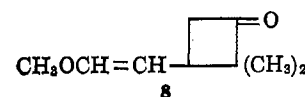


4 appears as two closely associated broad peaks, probably a set of *cis* and a set of *trans* isomers. The reaction of butylethylketene with 2-methyl-1,3-butadiene gave a 44% yield of a mixture of cyclobutanones, observed as four closely associated peaks in the gas-liquid partition chromatogram. These were probably sets of *cis* and *trans* isomers of the two structures 6 and 7.



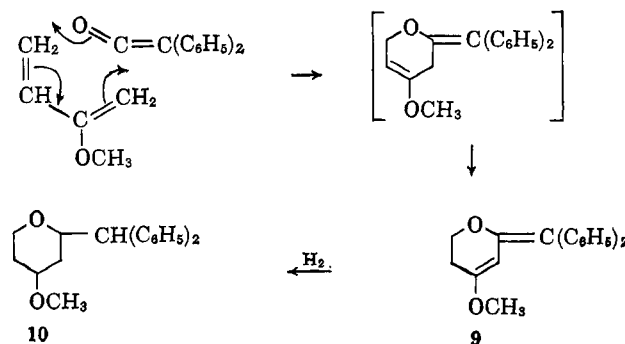
Introduction of a methoxy group at the 1-position of 1,3-butadiene produced a diene of greater reactivity than its parent. Dimethylketene reacted with 1,3-butadienyl methyl ether at room temperature in ethyl

ether solution to give the 1,2-cycloadduct, 3-(2-methoxyvinyl)-2,2-dimethylcyclobutanone (8) in 28% yield. Identification of 8 was based on a combination of elemental analysis and infrared and n.m.r. spectra.

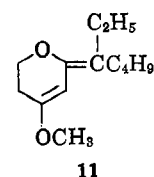


ether solution to give the 1,2-cycloadduct, 3-(2-methoxyvinyl)-2,2-dimethylcyclobutanone (8) in 28%

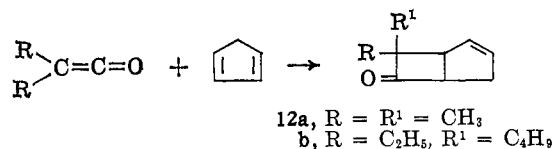
yield. Identification of 8 was based on a combination of elemental analysis and infrared and n.m.r. spectra. When a methoxy group was introduced at the 2 position of 1,3-butadiene, the resulting diene was less reactive with ketenes than was the 1 isomer. Methyl 1-methylenallyl ether also gave products of unusual structure when combined with certain ketenes. The reaction of methyl 1-methylenallyl ether with diphenylketene gave 5,6-dihydro-4-methoxy-2-diphenylmethylene-2H-pyran (9) in 25% yield. The following reactions show the formation of 9. The structure of 9 was assigned on the basis of elemental analysis, infrared and n.m.r. spectra, and catalytic hydrogenation to 10.



Butylethylketene and methyl 1-methylenallyl ether, when heated at 180°, gave 6-(1-ethylpentylidene)-5,6-dihydro-4-methoxy-2H-pyran (11) in 63% yield.



Previous workers observed that the reaction of cyclopentadiene with dimethylketene gave an adduct in yields ranging from 33%<sup>16,19</sup> to "nearly quantitative."<sup>17</sup> The last reference gave no experimental details. We found that cyclopentadiene was quite active as a cycloaddition partner. Dimethylketene and cyclopentadiene, when mixed in acetonitrile, gave a rapid, exothermic reaction that produced a high yield (84%) of the bicyclic ketone 12a. A good yield was also obtained by using hexane solvent although the reaction was slower. Butylethylketene and cyclopentadiene, when heated at 120° for 1 hr., gave an 82% yield of the ketone 12b.

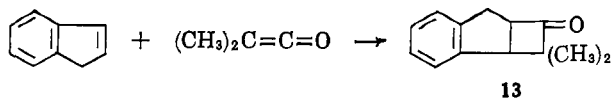


(25) Infrared spectra were recorded on a Baird AB-2 instrument.  
(26) N. m. r. spectra were recorded on a Varian A-60 instrument at 60 Mc. with tetramethylsilane as an internal standard.

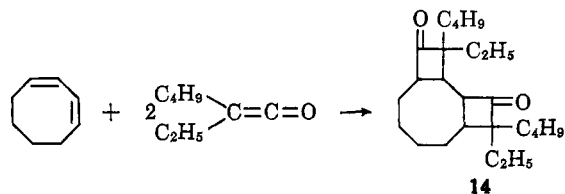
(27) K. B. Wiberg and B. J. Nist, *J. Am. Chem. Soc.*, **83**, 1228 (1961).

Indene and dimethylketene underwent a 1,2 cycloaddition at room temperature to give 1,2,2a,7a-tetra-

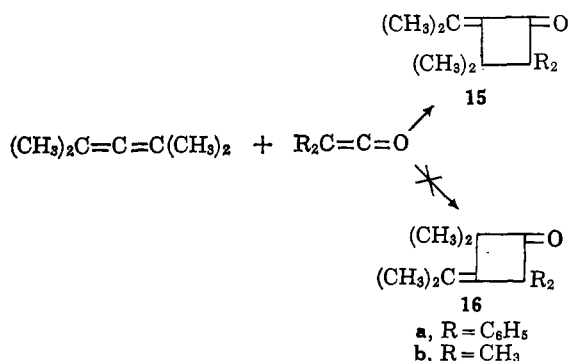
hydro-2,2-dimethyl-7H-cyclobut[*a*]inden-1-one (13) in 12% yield. 1,3-Cyclooctadiene and butylethylketene



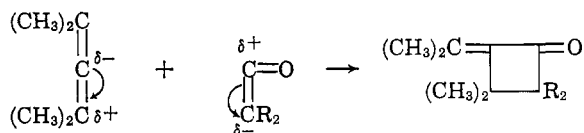
combined at 150° to produce a 15% yield of a 1,2 adduct that was a cyclobutanone of the possible structure 14.



The cumulative diene, 2,4-dimethyl-2,3-pentadiene, showed unexpected reactivity with ketenes. It reacted quite readily with diphenylketene and dimethylketene at room temperature to give 4-isopropylidene-3,3-dimethyl-2,2-diphenylcyclobutanone (15a) and 4-isopropylidene-2,2,3,3-tetramethylcyclobutanone (15b), respectively, in good yields. That these adducts did not possess the alternative structure 16 was proved



by the ultraviolet spectrum of 15b,  $\lambda_{\max}$  248  $m\mu$  ( $\epsilon$  12,267) and 348  $m\mu$  ( $\epsilon$  74), which is characteristic of an  $\alpha,\beta$ -unsaturated ketone. 16b would not be expected to exhibit a maximum at 248  $m\mu$ . In addition, the n.m.r. spectrum of 15b shows the four methyl groups attached to the ring as two peaks, while in structure 16b the four methyl groups are equivalent and would give only one peak. This unusual and facile cycloaddition indicates that 2,4-dimethyl-2,3-pentadiene exhibits the following polarization in cycloaddition reactions with ketenes. This mode of polariz-

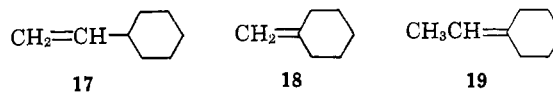


ation of the allene moiety is similar to that observed by Cripps, Williams, and Sharkey<sup>28</sup> in cycloaddition reactions of allenes with electron-deficient olefins.

In other papers of this series, we described the 1,2 cycloaddition of dialkylketenes to olefins substituted with electron-donating groups.<sup>1,24,29</sup> In this paper, we describe the 1,2 cycloaddition of butylethylketene

to olefins possessing no activating groups other than alkyl substituents.

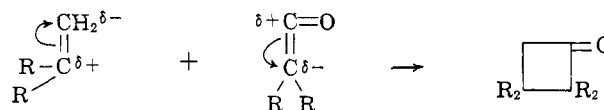
The reaction of diphenylketene with olefins to give cyclobutanones was reported previously.<sup>3-5,8,30-34</sup> Spengler<sup>34</sup> showed that diphenylketene forms adducts in high yields with olefins having terminal unsaturation. On the other hand, Van der Bij and Kooyman<sup>31</sup> observed that the olefin with terminal unsaturation (17) did not react with diphenylketene even at 100°, whereas olefins of types 18 and 19 did react. Staudinger<sup>7</sup> and Farmer and Farooq<sup>5</sup> reported that diphenylketene and cyclohexene did react, but that the addition required prolonged heating. Ziegler, *et al.*,<sup>33</sup> reported



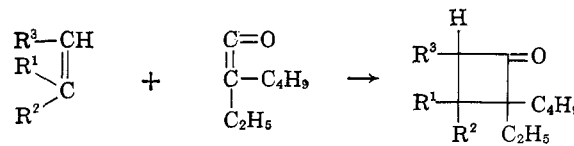
that one isomer of 1,5-cyclooctadiene, presumably the *trans,trans* form, reacted vigorously with diphenylketene.

Simple olefins are not very active in cycloaddition reactions with most ketenes. Dialkylketenes are not prone to undergo cycloaddition with unreactive partners; however, this lack of reactivity could possibly be overcome by the use of elevated temperatures. The competitive dimerization of the ketene must also be considered. Dimerization of dimethylketene is the predominant reaction when it is heated with olefins containing no functional groups. Bestian and Günther<sup>23</sup> were able to circumvent this problem by generating dimethylketene at elevated temperatures in the presence of an olefin. We found that butylethylketene, because of its low dimerization rate,<sup>24</sup> could successfully be forced into cycloaddition with olefins at elevated temperatures.

Olefins were found to give cyclobutanones with butylethylketene according to the following equation.



Butylethylketene and 2-methylpropene, when heated at 180° for 8 hr., afforded 2-butyl-2-ethyl-3,3-dimethylcyclobutanone (20a) in 42% yield. The structural assignment of this compound was based on infrared and n.m.r. spectra, and on analogy to the work of Bestian and Günther.<sup>23</sup> The infrared spectrum showed a carbonyl peak at 5.65  $\mu$ , characteristic of a cyclo-



- 20a,  $R^1 = R^2 = \text{CH}_3$ ;  $R^3 = \text{H}$   
 b,  $R^1 = \text{C}_6\text{H}_{13}$ ;  $R^2 = R^3 = \text{H}$   
 c,  $R^1 = \text{C}_{14}\text{H}_{29}$ ;  $R^2 = R^3 = \text{H}$   
 d,  $R^1 = \text{CH}_3$ ;  $R^2 = \text{H}$ ;  
 $R^3 = \text{C}_2\text{H}_5$

(30) H. Staudinger and E. Suter, *Chem. Ber.*, **53**, 1092 (1920).

(31) J. R. Van der Bij and E. C. Kooyman, *Rec. trav. chim.*, **71**, 837 (1952).

(32) M. O. Farooq and N. A. Abraham, *Bull. soc. chim. France*, 832 (1958).

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(29) R. H. Hasek and J. C. Martin, *J. Org. Chem.*, **28**, 1468 (1963).

TABLE I  
CYCLOBUTANONES FROM ACYCLIC OLEFINS AND DIALKYLKETENES

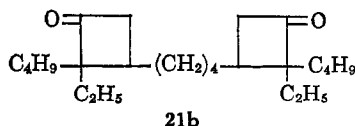
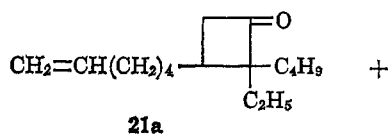
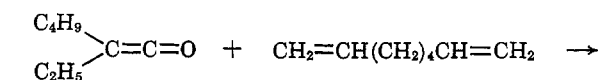
				B.p., °C. (mm.)	$n_D^{20}$	Yield, %	Formula	C, %		H, %	
R <sup>1</sup>	R <sup>2</sup>	R <sup>3</sup>	R <sup>4</sup>					Calcd.	Found	Calcd.	Found
CH <sub>3</sub>	CH <sub>3</sub>	C <sub>4</sub> H <sub>9</sub>	H	88-90 (6)	1.4510	42	C <sub>12</sub> H <sub>22</sub> O	79.2	79.3	12.1	12.0
<i>c</i> -C <sub>6</sub> H <sub>11</sub>	H	C <sub>4</sub> H <sub>9</sub>	H	135-137 (4)	1.4545	65	C <sub>18</sub> H <sub>30</sub> O	80.6	80.8	12.7	12.8
C <sub>14</sub> H <sub>29</sub>	H	C <sub>4</sub> H <sub>9</sub>	H	90-95 (1 <sup>a</sup> )	1.4613	66	C <sub>24</sub> H <sub>46</sub> O	82.2	82.2	13.2	13.2
C <sub>2</sub> H <sub>5</sub>	H	C <sub>4</sub> H <sub>9</sub>	CH <sub>3</sub>	80-84 (1.5)	...	39	C <sub>13</sub> H <sub>24</sub> O	79.5	79.8	12.3	12.2
CH <sub>3</sub>	CH <sub>3</sub>	(CH <sub>3</sub> ) <sub>2</sub> CHCH <sub>2</sub>	H	79 (5)	...	44	C <sub>12</sub> H <sub>22</sub> O	79.2	79.5	12.1	12.4

<sup>a</sup> Microns.

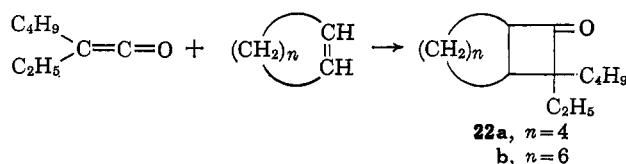
butanone; the n.m.r. spectrum showed the ring methylene group at 2.65 p.p.m., indicative of a methylene group adjacent to the carbonyl group of a cyclobutanone.<sup>27</sup>

Butylethylketene with 1-octene and 1-hexadecene, when heated at 180° for 8 hr., gave 2-butyl-2-ethyl-3-hexylcyclobutanone (**20b**, 80%) and 2-butyl-2-ethyl-3-tetradecylcyclobutanone (**20c**, 66%), respectively. Analysis by g.l.p.c. showed both of these materials to be mixtures of isomers. In several cases, *cis* and *trans* isomerism occurred in the cycloadducts, as shown by complex g.l.p.c. peaks. No attempts were made to separate pure isomers. The yields of **20b** and **20c** were higher than that of **20a**. This was probably due to more favorable steric factors. 2-Pentene, an olefin with internal unsaturation, and butylethylketene gave 2-butyl-2,4-diethyl-3-methylcyclobutanone (**20d**) in 39% yield. Ethylisobutylketene and 2-methylpropene, when heated at 180° for 6 hr., afforded 2-ethyl-2-isobutyl-3,3-dimethylcyclobutanone in 44% yield. A complete list of these products is given in Table I.

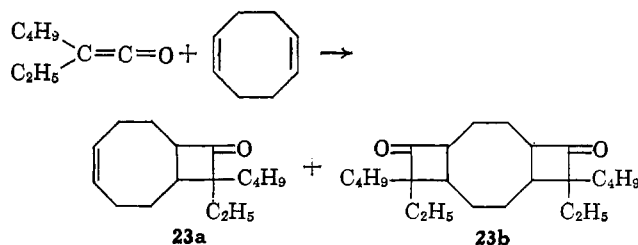
When 1,7-octadiene was heated with 2 moles of butylethylketene at 180° for 6 hr., the monoadduct **21a** was obtained in 47% yield and the diadduct **21b** was obtained in 18% yield.



Cyclic olefins also entered into cycloaddition with butylethylketene. Cyclohexene and cyclooctene reacted with butylethylketene to give the bicyclic adducts **22a** and **22b** in yields of 47 and 57%, respectively. When the nonconjugated cyclic diene 1,5-cyclooctadiene



was heated with 2 moles of butylethylketene, the monoadduct **23a** was obtained in 44% yield and the diadduct **23b** was obtained in 23% yield.



### Experimental Section

Indene, 1,3-butadienyl methyl ether, 1-octene, and 1-hexadecene were obtained from Aldrich Chemical Co., Inc.; cyclooctene, 1,3- and 1,5-cyclooctadiene, and 1,7-octadiene were obtained from Columbian Carbon Co.; 1,3-pentadiene and 2-methyl-1,3-butadiene were obtained from Matheson Coleman and Bell Division, Matheson Co., Inc.; 2-pentene was obtained from Columbia Organic Chemicals Co., Inc.; methyl 1-methylenallyl ether was obtained from Union Carbide Olefins Co. Diphenylketene was prepared by dehydrohalogenation of diphenylacetyl chloride,<sup>35</sup> and the dialkylketenes were prepared by pyrolysis of the corresponding anhydrides.<sup>36</sup> 2,4-Dimethyl-2,3-pentadiene was prepared by pyrolysis of 3-hydroxy-2,2,4-trimethyl-3-pentenoic acid,  $\beta$ -lactone.<sup>37</sup>

**2-Butyl-2-ethyl-3-vinylcyclobutanone (1).**—A mixture of 630 g. (5.0 moles) of butylethylketene and 540 g. (10.0 moles) of 1,3-butadiene was heated in an autoclave at 150° for 24 hr. Distillation of the reaction solution through a 12-in. packed column gave 401 g. (45%) of **1**: b.p. 77° (2.3 mm.);  $n_D^{20}$  1.4629; infrared absorptions (smear)<sup>28</sup> 5.62 (s), 6.12 (w), and 9.98 (s)  $\mu$ ; n.m.r. spectrum (CCl<sub>4</sub>)<sup>26</sup>: multiplet at 6.00 (—CH=C<), multiplet at 5.14 (>C=CH<sub>2</sub>), strong single peak in center of small multiple peaks at 2.90 —C(=O)CH<sub>2</sub>— and —CH—, multiple peaks at 1.34 (methylene groups), and multiple peaks at 0.89 (methyl groups) p.p.m. The respective area ratios of these peaks were 1:2:3:8:6. *Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>O: C, 79.9; H, 11.2. Found: C, 79.6; H, 11.2.

**2-Butyl-2-ethyl-3-propenylcyclobutanone (4).**—A mixture of 50.5 g. (0.4 mole) of butylethylketene and 54.5 g. (0.8 mole) of 1,3-pentadiene was heated in an autoclave at 150° for 24 hr. Distillation of the reaction solution through a 12-in. packed column gave 50.0 g. (64%) of **4**: b.p. 67-71° (0.75 mm.);  $n_D^{20}$  1.4658; infrared absorptions (smear): 5.62 (s), 6.0 (very weak), and 10.3 (m)  $\mu$ ; n.m.r. spectrum (neat): multiplet at 5.69 (—CH=CH—), strong single peak and multiple small peaks at 2.94 [—CH<sub>2</sub>C(=O)—, —CH—], doublet at 1.72 (CH<sub>3</sub>C=C<), multiple peaks at 1.40 (methylene groups), and multiple peaks at 0.89 (methyl groups) p.p.m. The area ratios of these peaks were 2:3:3:8:6, respectively.

(35) H. Staudinger, *Ber.*, **40**, 1148 (1907).

(36) R. H. Hasek and E. U. Elam (to Eastman Kodak Co.), Canadian Patent 618,772 (1961).

(37) J. C. Martin (to Eastman Kodak Co.), U. S. Patent 3,131,234 (1964).

*Anal.* Calcd. for  $C_{13}H_{22}O$ : C, 80.4; H, 11.4. Found: C, 80.0; H, 11.3.

**3-(2-Methoxyvinyl)-2,2-dimethylcyclobutanone (8).**—Under a nitrogen atmosphere, 84.0 g. (1.2 moles) of dimethylketene was added with stirring to a solution of 101.0 g. (1.2 moles) of 1,3-butadienyl methyl ether in 300 ml. of ethyl ether, over a period of 15 min. The solution was stirred for 18 hr. at room temperature and then distilled through a 10-in. packed column to give unchanged 1,3-butadienyl methyl ether, tetramethyl-1,3-cyclobutanedione, and 52.0 g. (28%) of **8**: b.p. 88–90° (9.5 mm.);  $n_D^{20}$  1.4646; infrared absorptions (smear): 5.67 (s) and 6.08 (s)  $\mu$ ; n.m.r. spectrum (neat): doublet at 6.50 ( $-\text{OCH}=\text{C}$ ), pair of doublets at 4.75 ( $\text{OC}=\text{CH}$ ), singlet at 3.45 (methoxy group), multiple peaks at 2.88 ( $>\text{CHCH}_2-$ ), and single peaks at 0.97 and 1.12 (methyl groups) p.p.m. The area ratios of these peaks were 1:1:3:3:6.

*Anal.* Calcd. for  $C_9H_{14}O_2$ : C, 70.1; H, 9.2; mol. wt., 154.2. Found: C, 69.9; H, 9.3; mol. wt. (ebullioscopic in benzene), 152.6.

**5,6-Dihydro-4-methoxy-2-diphenylmethylene-2H-pyran (9).**—A mixture of 8.4 g. (0.1 mole) of methyl 1-methyleallyl ether and 19.4 g. (0.1 mole) of diphenylketene was stirred in a small flask under a nitrogen atmosphere. The reaction temperature of the exothermic reaction was kept at 20–35° by means of a water bath. The mixture solidified after 12 hr. and, after two wasteful recrystallizations from a mixture of benzene and hexane, gave 7.0 g. of **9**: m.p. 132–133°; infrared absorptions (KBr): 6.14 (s) and 6.30 (s)  $\mu$ ; n.m.r. spectrum ( $\text{CCl}_4$ ): multiplet at 7.17 (aromatic protons), singlet at 5.24 (olefinic proton), triplet at 4.08 (ring methylene adjacent to oxygen), singlet at 3.42 (methoxy group), and triplet at 2.33 (other ring methylene) p.p.m. The area ratios of these peaks were 10:1:2:3:2.

*Anal.* Calcd. for  $C_{19}H_{18}O_2$ : C, 82.0; H, 6.5; mol. wt., 278.3. Found: C, 82.2; H, 6.3; mol. wt. (ebullioscopic in benzene), 283.

**Hydrogenation of 9.**—A 1-g. (0.0036-mole) sample of **9** in 30 ml. of ethyl acetate was hydrogenated over 0.5 g. of 5% palladium on carbon at room temperature and 45 p.s.i. in a pressure bottle equipped with a magnetic stirrer. A total of 0.00775 mole of hydrogen was absorbed over a period of 4 hr. The reaction mixture was filtered to remove the catalyst and the solvent was evaporated *in vacuo*. The residue was crystallized from hexane to give 0.7 g. of 2-(diphenylmethyl)tetrahydro-4-methoxypyran (**10**): m.p. 120–122°; infrared absorptions (KBr): complete absence of bands at 5.81 and 6.05  $\mu$  which were present in **9**; n.m.r. spectrum ( $\text{CH}_2\text{Cl}_2$ ): quite complex, however, multiplet at 7.12 (aromatic protons), complex multiplet at 3.5 ( $>\text{CH}-\text{O}$ ),

$-\text{CH}_2-\text{O}-$ ,  $-\text{O}-\text{CH}-\text{CH}$ , singlet at 3.11 (methoxy group), and multiplet at 1.5 (two methylene groups) p.p.m. These peak areas were in the ratio of 10:5:3:4.

*Anal.* Calcd. for  $C_{19}H_{22}O_2$ : C, 80.8; H, 7.9. Found: C, 80.7; H, 7.9.

**6-(1-Ethylpentylidene)-5,6-dihydro-4-methoxy-2H-pyran (11).**—A mixture of 63.0 g. (0.75 mole) of methyl 1-methyleallyl ether and 63.0 g. (0.5 mole) of butylethylketene was heated in an autoclave at 180° for 8 hr. Distillation of the reaction solution through a 12-in. packed column gave 73 g. of **11** (estimated purity 90% by g.l.p.c.), b.p. 80–83° (0.4 mm.). A sample for analysis was obtained as a center cut from distillation through a 24-in. spinning-band column. It boiled at 86° (0.7 mm.);  $n_D^{20}$  1.4834; infrared absorptions (smear): 5.95 and 6.05 (shoulder)  $\mu$ ; n.m.r. spectrum (neat): closely spaced triplet at 4.59 (olefinic proton), closely spaced quintet at 4.25 (methylene group adjacent to oxygen), singlet at 3.46 (methoxy group), broad peak at 2.81 (other ring methylene group), multiplet at 2.04 (methylene groups adjacent to double bond), multiplet at 1.30 (remaining methylene groups), and two triplets at 0.93 (methyl groups) p.p.m. These peak areas were in the ratio of 1:2:3:2:4:4:6.

*Anal.* Calcd. for  $C_{13}H_{22}O_2$ : C, 74.2; H, 10.5; mol. wt., 210.3. Found: C, 74.3; H, 10.4; mol. wt. (ebullioscopic in benzene), 216.

**7,7-Dimethylbicyclo[3.2.0]hept-2-en-6-one (12a).**—Under a nitrogen atmosphere, 35 g. (0.5 mole) of dimethylketene was added to a stirred solution of 33 g. (0.5 mole) of cyclopentadiene in 100 ml. of acetonitrile, over a period of 10 min. The reaction was quite exothermic and the temperature rose to 46° even with constant cooling by an ice bath. The temperature subsided

after about 30 min., and the reaction solution was stirred at room temperature for an additional 2 hr. Distillation of the reaction solution through a 12-in. packed column gave 56 g. (82%) of **12a**: b.p. 73° (21 mm.);  $n_D^{20}$  1.4726; infrared absorptions (smear): 5.63 (s) and 6.24 (w)  $\mu$ ; n.m.r. spectrum (neat): multiplet at 5.88 ( $-\text{CH}=\text{CH}-$ ), pair of triplets at 4.01 ( $>\text{CH}-\text{C}(=\text{O})-$ ), broad doublet at 3.20 ( $>\text{CH}-$ ), closely spaced doublet at 2.43 (methylene group), singlet at 1.28 (methyl group), and singlet at 0.93 (methyl group) p.p.m. These peak areas were in the ratio of 2:1:1:2:3:3.

**7-Butyl-7-ethylbicyclo[3.2.0]hept-2-en-6-one (12b).**—A 63-g. (0.5-mole) sample of butylethylketene and 33.0 g. (0.5 mole) of cyclopentadiene were mixed at room temperature under a nitrogen atmosphere. After 1 hr. the temperature had risen to 32°. The solution was heated at 120° for 1 hr. and distilled through a 10-in. packed column to give 10.0 g. of unchanged butylethylketene and 78.3 g. (82%) of **12b**, b.p. 85–89° (1.2 mm.),  $n_D^{20}$  1.4782, infrared absorptions (smear) at 5.63 (s) and 6.21 (w)  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{20}O$ : C, 81.2; H, 10.5. Found: C, 80.9; H, 10.7.

**1,2,2a,7a-Tetrahydro-2,2-dimethyl-7H-cyclobut[*a*]inden-1-one (13).**—Under a nitrogen atmosphere, 70.0 g. (1.0 mole) of dimethylketene was added with stirring to a solution of 116.0 g. (1.0 mole) of indene in 300 ml. of hexane, over a period of 15 min. No heat of reaction was observed. The solution stood at room temperature for 20 hr. and the low-boiling materials were removed by distillation up to a pot temperature of 185°. A considerable amount of unchanged dimethylketene dimer was recovered. On cooling, the residue was filtered to remove tetramethyl-1,3-cyclobutanedione and distilled through a 10-in. packed column to give unchanged indene and 22.0 g. (12%) of **13**, b.p. 101° (1.5 mm.). This material solidified on cooling and was recrystallized from hexane to give 17.2 g., m.p. 60.5–62°, infrared absorption (smear on heated plates) at 5.67  $\mu$ .

*Anal.* Calcd. for  $C_{13}H_{14}O$ : C, 83.8; H, 7.6. Found: C, 83.6; H, 7.2.

**4,12-Dibutyl-4,12-diethyltricyclo[8.2.0.0<sup>2,5</sup>]dodecane-3,11-dione (14).**—A mixture of 43.0 g. (0.4 mole) of 1,3-cyclooctadiene and 50.0 g. (0.4 mole) of butylethylketene was heated in an autoclave at 150° for 24 hr. Distillation of the reaction mixture through a 6-in. Vigreux column gave 38.0 g. of unchanged 1,3-cyclooctadiene, 40.0 g. of 2,4-dibutyl-2,4-diethyl-1,3-cyclobutanedione, and 11.0 g. (15%) of **14**, b.p. 155–160° (0.08 mm.), infrared absorption (smear) at 5.66 (s)  $\mu$ ; the n.m.r. spectrum was rather complex, but showed no olefinic protons.

*Anal.* Calcd. for  $C_{24}H_{40}O_2$ : C, 80.0; H, 11.2; mol. wt., 360.0. Found: C, 79.9; H, 11.4; mol. wt. (ebullioscopic in benzene), 342.

**4-Isopropylidene-3,3-dimethyl-2,2-diphenylcyclobutanone (15a).**—A mixture of 20.2 g. (0.104 mole) of diphenylketene and 10.0 g. (0.104 mole) of 2,4-dimethyl-2,3-pentadiene was stirred at room temperature under a nitrogen atmosphere. The resulting exothermic reaction was kept at 25–30° by an ice bath. The reaction mixture solidified after 30 min. and was recrystallized from ethyl acetate to give 22.0 g. (73%) of **15a**, m.p. 137–139°, infrared absorptions (KBr) at 5.81 (s) and 6.05 (s)  $\mu$ .

*Anal.* Calcd. for  $C_{21}H_{22}O$ : C, 86.9; H, 7.6; mol. wt., 290.4. Found: C, 86.6; H, 7.7; mol. wt. (ebullioscopic in benzene), 284.

**4-Isopropylidene-2,2,3,3-tetramethylcyclobutanone (15).**—When 48.0 g. (0.5 mole) of 2,4-dimethyl-2,3-pentadiene and 17.5 g. (0.25 mole) of dimethylketene were mixed with stirring at room temperature under a nitrogen atmosphere, the temperature of the reaction solution slowly rose to 38°. After having been stirred for 8 hr., the solution was distilled through a 6-in. Vigreux column to give 28.0 g. (68%) of **15b**: b.p. 45° (0.5 mm.);  $n_D^{20}$  1.4778; ultraviolet absorptions (isopropyl alcohol):  $\lambda_{\text{max}}$  248 m $\mu$  ( $\epsilon$  12,267) and 348 m $\mu$  ( $\epsilon$  74); infrared absorptions (smear): 5.78 (s) and 6.05 (s)  $\mu$ ; n.m.r. spectrum (neat): two peaks at 1.98 and 1.77 [ $(\text{CH}_3)_2\text{C}=\text{C}$ ], singlet at 1.25 [ $-\text{C}(=\text{O})-\text{C}(\text{CH}_3)_2-$ ], and singlet at 1.00 [ $(\text{CH}_3)_2\text{C}-\text{C}=\text{C}$ ] p.p.m.

*Anal.* Calcd. for  $C_{11}H_{18}O$ : C, 79.5; H, 10.8. Found: C, 79.2; H, 10.8.

**2-Butyl-2-ethyl-3,3-dimethylcyclobutanone (20a).**—A mixture of 252 g. (2.0 moles) of butylethylketene and 336 g. (6.0 moles) of 2-methylpropene was heated in an autoclave at 180° for 8 hr. Distillation of the reaction mixture through a 12-in. packed column gave 151 g. (42%) of **20a**: b.p. 88–90° (6 mm.);  $n_D^{20}$  1.4510; infrared absorption (smear): 5.65  $\mu$ ; n.m.r. spectrum

(CCl<sub>4</sub>): multiple peaks from 0.70 to 1.08 (side-chain methyl groups) and from 1.08 to 1.88 (methylene groups), singlet at 1.22 (ring methyl groups), and singlet at 2.66 (ring methylene group) p.p.m.

*Anal.* Calcd. for C<sub>12</sub>H<sub>20</sub>O: C, 79.2; H, 12.1. Found: C, 79.3; H, 12.0.

**2-Butyl-2-ethyl-3-(5-hexenyl)cyclobutanone (21a) and 3,3'-Tetramethylenebis[2-butyl-2-ethylcyclobutanone] (21b).**—A mixture of 30 g. (0.27 mole) of 1,7-octadiene and 76 g. (0.6 mole) of butylethylketene was heated at 180° for 6 hr. Distillation of this solution through a 12-in. packed column afforded 5 g. of unchanged 1,7-octadiene, 30.5 g. (47%) of 21a, b.p. 121° (1.6 mm.), *n*<sub>D</sub><sup>20</sup> 1.4628, and 17.6 g. (18%) of 21b, b.p. 178° (0.2 mm.).

21a had infrared absorptions (smear) at 5.67 and 6.11 μ; n.m.r. spectrum (neat): multiplet at 0.94 (methyl groups), broad multiplets from 1.10 to 2.30 (methylene groups), ring methylene group consisting of two chemically different protons, the first as a pair of doublets at 2.58 (*J* = 17.1 and 6.9 c.p.s.) and the second as a pair of doublets at 3.05 (*J* = 17.1 and 9.0 c.p.s.), and complex multiplets at 5.04 and 5.83 (vinyl group) p.p.m.

*Anal.* Calcd. for C<sub>18</sub>H<sub>28</sub>O: C, 81.3; H, 11.9. Found: C, 81.4; H, 11.8.

21b had infrared absorption (smear) at 5.67 μ; n.m.r. spectrum (neat): triplet at 0.92 (methyl groups), multiplet at 1.45 multiplet at 1.45 (methylene groups), broad peak at 2.10 (methylidyne protons), and two equivalent ring methylene each consisting of two chemically different protons, the first as pair of doublets at 2.59 (*J* = 17.1 and 7.0 c.p.s.), and the second as a pair of doublets at 3.04 (*J* = 17.1 and 8.9 c.p.s.) p.p.m.

*Anal.* Calcd. for C<sub>24</sub>H<sub>40</sub>O<sub>2</sub>: C, 79.5; H, 11.7. Found: C, 79.6; H, 11.7.

**8-Butyl-8-ethylbicyclo[4.2.0]octan-7-one (22a).**—A mixture of 63 g. (0.5 mole) of butylethylketene and 164 g. (2.0 moles) of cyclohexene was heated at 180° for 12 hr. Distillation of the

reaction solution through a 12-in. packed column gave 132 g. of unchanged cyclohexene and 71 g. of a material boiling at 90–93° (0.75 mm.). Analysis by g.l.p.c. showed this distillate to be a mixture containing 31% of butylethylketene dimer and 69% of 22a. Pure 22a was separated by g.l.p.c.: infrared absorption (smear) at 5.65 μ.

*Anal.* Calcd. for C<sub>14</sub>H<sub>24</sub>O: C, 80.8; H, 11.5. Found: C, 80.7; H, 11.5.

**10-Butyl-10-ethylbicyclo[6.2.0]decan-9-one (22b).**—A mixture of 34.0 g. (0.27 mole) of butylethylketene and 57.0 g. (0.52 mole) of cyclooctene was heated in an autoclave at 180° for 8 hr. Analysis by g.l.p.c. indicated the high-boiling portion of the reaction mixture to be 30% butylethylketene dimer and 70% new product 22b. Distillation through a 12-in. packed column gave 37 g. of unchanged cyclooctene and 35.8 g. (57%) of 22b, b.p. 113–115° (0.9 mm.), *n*<sub>D</sub><sup>20</sup> 1.4854.

*Anal.* Calcd. for C<sub>16</sub>H<sub>28</sub>O: C, 81.3; H, 11.9. Found: C, 81.2; H, 11.9.

**10-Butyl-10-ethylbicyclo[6.2.0]dec-4-en-9-one (23a) and 6,11-Dibutyl-6,11-diethyltricyclo[8.2.0<sup>4,7</sup>]dodecane-5,12-dione (23b).**—A mixture of 68.0 g. (0.54 mole) of butylethylketene and 29.3 g. (0.27 mole) of 1,5-cyclooctadiene was heated in an autoclave at 180° for 8 hr. Distillation of the resulting solution through a 12-in. packed column gave 7 g. of unchanged 1,5-cyclooctadiene, 27.8 g. (44%) of 23a, b.p. 103–105° (0.4 mm.), *n*<sub>D</sub><sup>20</sup> 1.4918, and 22.0 g. (23%) of 23b, b.p. 198–199° (0.75 mm.), *n*<sub>D</sub><sup>20</sup> 1.4958.

23a had infrared absorptions (smear) at 5.69 and 6.1 μ; n.m.r. spectrum (neat): multiplet at 0.92 (methyl groups) and complex broad peaks from 1.10 to 2.50 (methylene groups), broad multiplet at 3.20 (>CHC(=O)–), and multiplet at 5.72 (olefinic protons) p.p.m.

*Anal.* Calcd. for C<sub>16</sub>H<sub>28</sub>O: C, 82.0; H, 11.2. Found: C, 81.7; H, 11.2.

23b had infrared absorption (smear) at 5.67 μ.

*Anal.* Calcd. for C<sub>24</sub>H<sub>40</sub>O<sub>2</sub>: C, 79.9; H, 11.2. Found: C, 79.4; H, 11.1.

## Alkylation of N,N-Dialkylarylamines with Tropylium Fluoroborate

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Alkylation of aromatic rings, activated by dialkylamino groups, occurred when tropylium fluoroborate was the alkylating agent. The products obtained were isomeric mixtures of dialkylaminoarylcycloheptatrienes resulting from double bond shifts in the seven-membered ring. Some of these isomers were isolated and their structures were established. The thermal isomerization of some 7-substituted 1,3,5-cycloheptatrienes was examined by n.m.r. spectroscopy. Oxidation of the substituted cycloheptatrienes to the corresponding tropylium salts occurred with triphenylmethyl fluoroborate, giving deep blue, stable compounds.

The presence of the hydroxyl<sup>1</sup> or methoxy<sup>2</sup> group on an aromatic ring allows electrophilic substitution by the tropylium ion, but benzene is not attacked.<sup>2</sup> Electrophilic substitution occurs with other cations (methylbenzo-1,3-dithiolium,<sup>3</sup> flavylum,<sup>4</sup> and phenyl-1,2-dithiolium<sup>5</sup>) when a dialkylamino group is present. These results suggested that the presence of a dialkylamino group on an aromatic ring would permit electrophilic substitution by the tropylium ion. Hydride abstraction from such substituted cycloheptatrienes might be expected to give resonance-stabilized colored cations. This suggestion has recently been verified by Jutz and Voithenleitner,<sup>6</sup> who found that N,N-dimethylaniline was alkylated in the *para* posi-

tion by methyl troyl ether and that the product was readily converted to a stable tropylium salt. This paper describes our findings when tropylium fluoroborate was the alkylating agent.

1-Dimethylaminonaphthalene (1a) was alkylated when treated with tropylium fluoroborate in acetonitrile at room temperature. The product (83%) has the correct elemental composition (C<sub>19</sub>H<sub>19</sub>N), but the n.m.r. spectrum has two groups of peaks in the τ 7 to 8 region (allylic seven-membered ring protons), indicating that it is a mixture of isomers differing in the position of substitution on the seven-membered ring. One isomer was isolated as the amine salt (23%) and found to be identical with the product obtained from 4-lithio-1-dimethylaminonaphthalene (1d) and tropylium fluoroborate. Thus, the seven-membered ring is attached to the 4 position of the naphthalene ring.

The n.m.r. spectrum of this amine established its structure as 3-(1-dimethylamino-4 naphthyl)-1,3,5-cy-

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