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Thermal Addition Reactions of Monocyclic Phenols with Ethylene

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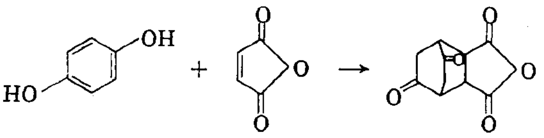
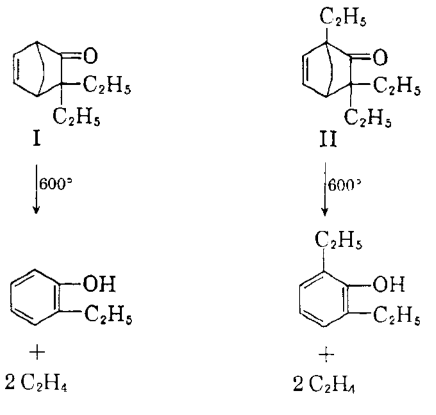
Ethyl-substituted bicyclooctenones have been obtained by the thermal addition of ethylene to monohydric phenols at high pressure. This ketone synthesis apparently involves *ortho* alkylation followed by the 1,4-addition of ethylene. Dihydric phenols react similarly to give cyclohexendiones and bicyclic ketones.

The first instance of a Diels-Alder reaction involving a monocyclic aromatic compound is that of hydroquinone with maleic anhydride to form 5,7 - dioxobicyclo[2.2.2]octane - 2,3 - dicarboxylic anhydride.[1] An analogous reaction has also been reported for 2,5-dimethylhydroquinone.[2] We wish to report here the nature of the products formed in reactions of monohydric and dihydric phenols with ethylene at high temperature and pressure.



Reactions with monohydric phenols. Phenol and ethylene at 275° and 3000 atm. have given in 57% conversion a mixture of bicyclo[2.2.2]octenones I (10%) and II (90%) derived by the combination of phenol with 3 and 4 moles of ethylene, respectively. The major phenolic product was 2,6-diethylphenol. The structures 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I) and 1,3,3-triethylbicyclo[2.2.2]oct-5-en-2-one (II) are in agreement with the elemental composition of the products and with their infrared, ultraviolet, and nuclear magnetic resonance spectra. These structures were established further by transformations of the ketones. Thus, I and II absorbed one mole equivalent of hydrogen to yield the corresponding bicyclooctanones, and the pyrolysis of I and II to obtain ethylene along with *o*-ethylphenol and 2,6-diethylphenol, respectively, has defined the nature of the bridge and the position of the alkyl groups. Furthermore, I and II were synthesized directly from ethylene and *o*-ethylphenol.



I II

Other monohydric phenols reacted similarly. 2,6-Dimethylphenol and ethylene gave a single ketone believed to be 1,3-dimethyl-3-ethylbicyclo[2.2.2]-oct-5-en-2-one (III) (Fig. 1) as judged by its elemental composition, spectral properties, and pyrolysis to regenerate 2,6-dimethylphenol. *o*-Cresol formed two products, the composition and spectra of which conformed to the structures 3-ethyl - 3 - methylbicyclo[2.2.2]oct - 5 - en - 2 - one (IV) and either 1,3-diethyl-3-methylbicyclo[2.2.2]-oct-5-en-2-one (V) or the isomeric 3,3-diethyl-1-methylbicyclo[2.2.2]oct-5-en-2-one (VI).

In the conversion of monohydric phenols to bicyclooctenones by reaction with ethylene, it

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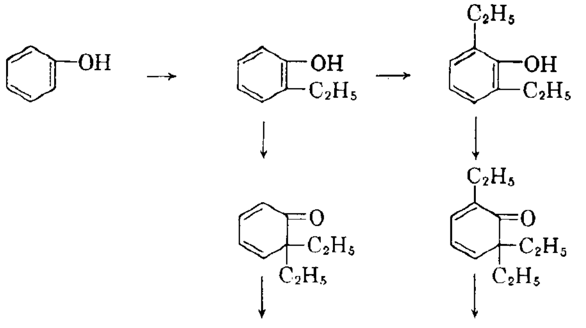
[1] R. C. Cookson and N. S. Wariyar, *Chem. & Ind.*, 915 (1955); *J. Chem. Soc.*, 327 (1957).

[2] K. Takeda and K. Kitahonoti, *Ann.*, **606**, 153 (1957).

appears likely that *ortho* alkylation proceeded until one *ortho*-position had been alkylated twice, and the resulting cyclohexadienones then underwent Diels-Alder addition. Thus, the following scheme is proposed.



I

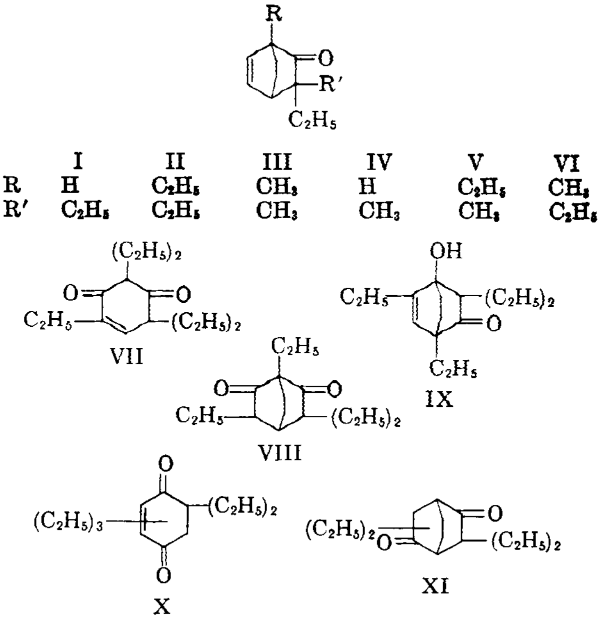
II

This scheme is in accord with the following considerations: (a) *o*-alkylphenols have been reported as the major product of the uncatalyzed reaction of phenol with olefins at 325° and 100–250 atm.[3] using an olefin/phenol mole ratio of approximately 2; (b) the bicyclooctenone II did not revert to a phenol when heated at its boiling point (270°). Thus, the formation of alkylphenols by decomposition of bicyclooctenones at the synthesis temperature (275°) is very unlikely; (c) the preponderance of ketone II over ketone I is in accord with the isolation of 2,6-diethylphenol as the major phenolic component.

Propylene with phenol at 275° and 3000 atm. afforded 2,6-diisopropylphenol as the major product (65% conversion to crude) with little other phenolic material. The infrared spectrum of the relatively small neutral fraction showed the absence of ketone. Similar results were obtained with isobutylene which afforded 2-*t*-butylphenol (29% conversion to crude) and 2,6-di-*t*-butylphenol (28% conversion to crude) and no ketone. The failure of propylene and isobutylene to give ketone products analogous to those obtained from ethylene is undoubtedly due to steric factors.

The aluminum phenoxide-catalyzed *ortho* and *diortho* alkylation of phenols has recently been reported.[4] Our results show that 2,6-dialkylphenols rather than the 2,4-isomers are preferentially formed even in the absence of a catalyst. In contrast to the catalyzed reaction, in which ethylene was found to be much less reactive than either propylene or isobutylene, the reactivity of these olefins under our conditions is of the same order of magnitude (with ethylene being unique in its ability to react further to form bicyclic ketones). In the uncatalyzed thermal alkylation of phenols reported earlier,[3] in which *o*-alkylphenols were the major product (olefin was not repressured into the system as the reaction proceeded), it was also found that the reactivity of ethylene was comparable to that of other olefins. However, in contrast to our results, the diethylphenol obtained from phenol and ethylene was reported to probably be the 2,4-isomer. The formation of bicyclooctenones from phenols and ethylene appears to be clearly the effect of high pressure since the temperatures used in our work and in the aluminum phenoxide-catalyzed reactions are comparable.

Reactions with dihydric phenols. Resorcinol gave in 55% yield a product $C_{16}H_{26}O_2$ which appeared to consist of three isomeric ketones. The major component (60% of the total) was a conjugated ketone for which the structure 1,1,3,3,5-pentaethyl-4-cyclohexen-2,6-dione (VII) (Fig. 1) is proposed. A second fraction, representing 30% of the ketone product, appeared on the basis of its analysis and infrared spectrum to be a mixture of an isomeric ($C_{16}H_{26}O_2$) diketone and hydroxy ketone for which the structures 1,3,3,5-tetraethylbicyclo[2.2.2]-octane-2,6-dione (VIII) and 1-hydroxy-2,2,4,6-tetraethylbicyclo[2.2.2]oct-5-en-3-one (IX) are proposed, respectively. The assignment of these structures is based on physical data and the assumption that alkylation occurs *ortho* to the hydroxyl groups as observed with monohydric phenols.



	I	II	III	IV	V	VI
R	H	C_2H_5	CH_3	H	C_2H_5	CH_3
R′	C_2H_5	C_2H_5	CH_3	CH_3	CH_3	C_2H_5

Fig. 1. Products from the reaction of monocyclic phenols with ethylene

The major products (in 55% yield) from hydroquinone and ethylene were largely isomeric $C_{16}H_{26}O_2$ ketones which were difficult to separate by distillation. The lower boiling C_{16} fractions were mostly conjugated ketones for which the partial structure pentaethyl-2-cyclohexen-1,4-dione (X) is proposed. The remaining C_{16} fractions were chiefly isomeric

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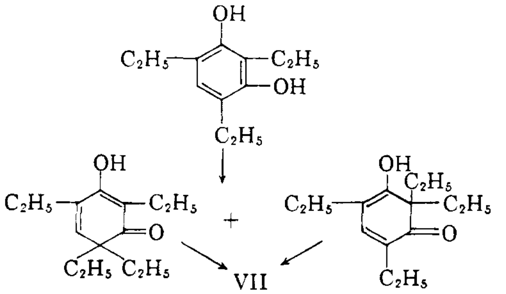
(3) E. A. Goldsmith, M. J. Schlatter, and W. G. Toland, *J. Org. Chem.*, **23**, 1871 (1958).

(4) A. J. Kolka, J. P. Napolitano, A. H. Filbey, and G. G. Ecke, *J. Org. Chem.*, **22**, 642 (1957). R. Stroh, R. Seydel, and W. Hahn, *Angew. Chem.*, **69**, 699 (1957).

unconjugated ketones, which absorbed strongly in the infrared at 11.95 μ and for which the tetraethylbicyclo[2.2.2]octane-2,5-dione structure (XI) is proposed. A small proportion of $C_{18}H_{30}O_2$ ketone was also obtained. Although the C_{18} ketone was unconjugated, it did not appear to be bicyclic as judged from its infrared and ultraviolet spectra which were quite different from those of XI.

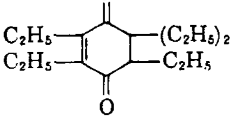
Catechol and ethylene formed ketone products (in 35% yield) which on distillation gave a constant boiling fraction (*ca.* 50% of total product) of the composition $C_{14}H_{22}O_2$. The infrared spectrum of this material showed absorption due to hydroxyl and to unconjugated and also conjugated carbonyl groups, indicating a mixture of at least two compounds. The presence in the product of a triethyl hydroxybicyclooctenone ($C_{14}H_{22}O_2$) would be consistent with the behavior of the simple phenols and with the spectroscopic data.

The reactions of dihydric phenols with ethylene can be rationalized in a manner very similar to that for the monohydric phenols. Thus, if one postulates in the case of resorcinol the preferential alkylation of all *ortho-* positions followed by the double alkylation of one *ortho-* position, the following scheme results, and the difference in the mode of reaction of resorcinol and of phenol involves only the ability of the proposed enol intermediates VIIIa and IXa either to undergo further *ortho* alkylation or to add ethylene.



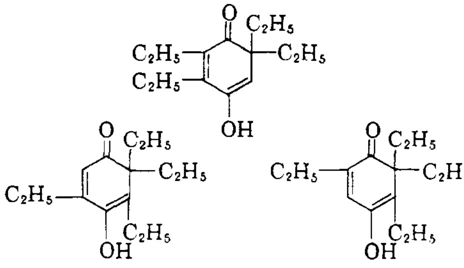
VIII ← VIIIa IXa → IX

Similarly, hydroquinone and ethylene might be expected to yield principally the pentaethylcyclohexendione Xa, with tetraethylhydroquinone as the intermediate. However, the presence of a substantial amount of isomeric C_{16} unconjugated



Xa

ketones (bicyclooctanediones) in addition to pentaethylcyclohexendione suggests that such C_{14} intermediates as the following either undergo further *ortho* alkylation to give pentaethylcyclohexendiones (X) or add ethylene to give tetraethylbicyclooctanediones (XI).



EXPERIMENTAL

The preparation of bicyclooctenones[5] was carried out by heating the phenol with ethylene at high pressures in an oxygen-free system. The phenol was introduced into a 200 ml. pressure vessel which was equipped with a rocker mechanism and which was evacuated and purged with oxygen-free nitrogen. The vessel and its contents were shaken and heated while the ethylene was injected intermittently as required to maintain the pressure level for the duration of the reaction time (13–16 hr.). The reaction products were triturated with pentane, and the pentane solution was filtered and then extracted with four 200-ml. portions of aqueous methanolic potassium hydroxide.[6] After the pentane solution had been washed once with water, it was dried over anhydrous calcium sulfate and filtered. The residue obtained on removal of the pentane was then distilled under reduced pressure to obtain the ketonic products for fractionation. As an alternative, the crude product may first be distilled and then extracted with alkali.

The aqueous methanolic potassium hydroxide extracts were diluted with water, cooled, and strongly acidified. The phenolic products liberated were extracted with pentane, and the pentane solution was dried over anhydrous calcium sulfate, filtered and distilled to obtain the phenols.

Characterization of the products from phenol and ethylene. The crude product (251 g.) obtained by reaction of ethylene at 275° and 2600–3000 atm. with 120 g. of phenol (three runs of 40 g. each) afforded, after the removal of phenolic material, 124 g. (48% conversion[7]) of ketone product, b.p. 65–78° (0.3 mm.); n_D^{25} 1.4885. Fractionation of this product in a Podbielniak column gave 10 ml. of 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I); b.p. 130.5° (20 mm.); n_D^{25} 1.4935; d_{25} 0.9968; and 85 ml. of 1,3,3-triethylbicyclo[2.2.2]oct-5-en-2-one (II); b.p. 270° (760 mm.), 144.5° (20 mm.); n_D^{25} 1.4878–1.4882; d_{25} 0.9825. An additional 14 ml. of ketone II was obtained as a distillation residue; n_D^{25} 1.4883. These ketones have a camphoraceous odor.

Anal. Calcd. for $C_{12}H_{18}O$ (I): C, 80.85; H, 10.18. Found: C, 80.65; H, 10.18.

Anal. Calcd. for $C_{14}H_{22}O$ (II): C, 81.50; H, 10.75. Found: C, 81.63; H, 10.80.

Treatment of the crude ketone product with 2,4-dinitrophenylhydrazine in 95% alcohol containing a little sulfuric acid gave a crystalline derivative; m.p. 148–162°. After two recrystallizations from ethanol, the melting point was 165.5–168°. (The derivative obtained from a different sample gave the m.p. 170–170.5° after several recrystallizations.) This was the 2,4-dinitrophenylhydrazone of 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I).

Anal. Calcd. for $C_{18}H_{22}N_4O_4$: C, 60.32; H, 6.19; N, 15.63. Found: C, 59.90; H, 6.12; N, 15.86 (m.p. 165.5–168°).

The infrared, ultraviolet,[8] and nmr spectra of the pure

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[5] Thomas J. Kealy, U. S. Patent 2,883,425, April 21, 1959.

[6] The alkali (Claisen's) was prepared as described by D. S. Tarbell, J. W. Wilson, and P. E. Fonta, *Org. Syntheses*, Coll. Vol. III, 269 (1955).

[7] Conversions to ketone were as high as 57%.

[8] The ultraviolet spectra of all the ketone products were measured in absolute ethyl alcohol, and the ultraviolet spectra of the phenols were measured in cyclohexane.

ketones were in accord with structure I and II; =CH 3.3 μ, unconjugated >C=O 5.8 μ (ketone I), 5.85 μ (ketone II), strained C=C 6.2 μ; λ_{max} 300 mμ, ε 98.1 (ketone I), λ_{max} 302 mμ, ε 103 (ketone II). The nmr spectrum of ketone I (measured at 56.4 Mc, relative to tetramethylsilane) showed doublets of equal area centered at −166 and −151 cps. assigned to the bridgehead hydrogens. Two sets of three peaks each were centered at −363 and −339 cps. These were assigned to the two non-equivalent olefinic hydrogens which interact with each other and with the bridgehead hydrogens. The area under the peaks of the bridgehead hydrogens equaled the area under the olefinic hydrogen peaks. Ketone II showed one doublet centered at −148 cps. assigned to the bridgehead hydrogen, the area of which was approximately one-half that of the olefinic hydrogen peaks.

A 2,4-dinitrophenylhydrazone was not formed by the triethyl ketone II, which suggested that this ketone was more hindered than the diethyl ketone I.

Ketones I and II did not react with ethyl nitrite in the presence of sodium ethoxide, indicating the absence of active hydrogen and suggesting the presence of a *gem*-diethyl group *alpha* to the carbonyl group.

Hydrogenation confirmed the presence of only one double bond in each ketone.

Hydrogenation of ketone I. A solution of 2 g. of crude 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I) (n^{25}_{D} 1.4900) in 75 ml. of absolute ethanol was hydrogenated at room temperature under 40 lb./sq. in. of hydrogen using a platinum oxide catalyst. The pressure quickly decreased to the calculated amount for the absorption of 1 mole equivalent of hydrogen. No further uptake of hydrogen was observed during 60 hr. shaking at approximately 60°. The alcohol was removed, and a 0.5-g. portion of the product was treated with 2,4-dinitrophenylhydrazine for 20 hr. The solution was filtered to obtain 0.24 g. of the dinitrophenylhydrazone of 3,3-diethylbicyclo[2.2.2]octan-2-one, m.p. 178–183°. After three recrystallizations from absolute ethanol, the product melted at 190–190.5.

Anal. Calcd. for $C_{18}H_{24}O_4N_4$: C, 59.98; H, 6.71; N, 15.55. Found: C, 59.55; H, 6.85; N, 14.98.

Hydrogenation of ketone II. 1,3,3-Triethylbicyclo[2.2.2]-oct-5-en-2-one (II) (20 g., n^{25}_{D} 1.4880) in 80 ml. of absolute ethanol was hydrogenated at room temperature using a 10% palladium-on-carbon catalyst and 40 lb./sq. in. hydrogen pressure. One mole equivalent of hydrogen was absorbed in about 15 min. After 3 hr., with no further absorption of hydrogen, the alcohol was removed under reduced pressure, and the 1,3,3-triethylbicyclo[2.2.2]octan-2-one was distilled; b.p. 73° (0.2 mm.); n^{25}_{D} 1.4839.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61. Found: C, 81.18; H, 11.81.

Identification of phenolic products. The phenolic fraction (65 ml.) collected from several experiments afforded on distillation (a) 10 ml., b p. 83–100° (15 mm.), n^{25}_{D} 1.5335–1.5249 probably containing phenol, *o*-ethylphenol and 2,6-diethylphenol,[9] (b) 37 ml. of 2,6-diethylphenol; b.p. 102° (15 mm.), m.p. 34.5–37°, λ_{max} 278, 271 mμ, ε 1770, 1725; and (c) 16 ml. of unidentified phenols; b.p. 111–127° (15 mm.), n^{25}_{D} 1.5149–1.5031. Fraction b was identified by analysis and by comparison of its infrared and ultraviolet spectra with those of authentic 2,6-diethylphenol,[10] m.p. 36–36.5°, λ_{max} 278, 271 mμ, ε 1815, 1755.

Pyrolysis of 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I). Ketone I (5 ml., n^{25}_{D} 1.4935) was passed through a tube 1 foot in length at 600° under 1 mm. pressure over a period of 20 min. The volatile pyrolysis product was shown by infrared inspection to consist chiefly of ethylene. The nonvolatile product was dissolved in pentane, and the solution was extracted with aqueous methanolic potassium hydroxide. After acidification of the alkaline extracts, the phenol was dissolved in pentane, and the solution was dried. Removal of the pentane gave *o*-ethylphenol which afforded a phenylurethan, m.p. 131.5–133°, having an infrared spectrum identical with that of the phenylurethan obtained from authentic *o*-ethylphenol, m.p. 136–138°.

Treatment of *o*-ethylphenol obtained as a pyrolysate with chloroacetic acid afforded *o*-ethylphenoxy acetic acid, m.p. 134–135°; the infrared spectrum of this derivative was identical with that of the derivative prepared from authentic *o*-ethylphenol, m.p. 136.5–138°.

Pyrolysis of 1,3,3-triethylbicyclo[2.2.2]oct-5-en-2-one (II). Ketone II (20 ml., n^{25}_{D} 1.4880) was passed through a tube 1 foot in length at 600° under 1 mm. pressure during a period of about 1 hr. Infrared analysis established that the volatile pyrolysis product was chiefly ethylene. The nonvolatile product was dissolved in pentane, and the solution was extracted with aqueous methanolic potassium hydroxide. The pentane on distillation left about 1 ml. of residue that was discarded. Acidification of the alkali solution gave a yellow oil which was extracted with pentane. The pentane solution was washed with water, dried, and evaporated on a steam bath to obtain an orange oil which on distillation gave 6.5 g. of colorless oil, b.p. 83–90° (5 mm.), n^{25}_{D} 1.5241–1.5231. A portion of the distilled product was dissolved in pentane. Cooling the solution in a solid carbon dioxide-acetone bath afforded 2,6-diethylphenol as white needles which were recrystallized several times by the same procedure; m.p. 36–36.5° alone or in admixture with authentic 2,6-diethylphenol. The identity of the product was further confirmed by a comparison of its infrared and ultraviolet spectra (λ_{max} 278, 271 mμ, ε 1770, 1710) with those of the authentic sample.

Synthesis of ketones I and II by reaction of o-ethylphenol with ethylene. o-Ethylphenol (23 g.) was heated with ethylene at 275° and 2700–3000 atm. for 13.5 hr. Separation of the phenolic material and distillation gave 12.5 g. (33% conversion) of ketone; b.p. 122–141° (17 mm.); n^{25}_{D} 1.4882. The infrared spectrum of this material showed that it consisted mostly of 1,3,3-triethylbicyclo[2.2.2]oct-5-en-2-one (II). Weak bands at 8.25 μ and at 11.7 μ indicated the presence of a small amount of 3,3-diethylbicyclo[2.2.2]oct-5-en-2-one (I) which was substantiated by the isolation of its 2,4-dinitrophenylhydrazone. One gram of the ketone product on treatment with 0.4 g. of reagent gave 0.05 g. of crude 2,4-dinitrophenylhydrazone; m.p. 159–161°. One recrystallization from ethanol raised the melting point to 166–168°.

Reaction of ethylene with 2,6-dimethylphenol. 2,6-Dimethylphenol (40 g.) was treated with ethylene at 275° and 2750–3000 atm. for 14 hr. After removal of grease and phenolic material, the product was distilled to obtain 30 g. (50% conversion) of water-white camphoraceous product, b.p. 42–43° (0.2 mm.); n^{25}_{D} 1.4829; d_{25} 0.9729. The infrared and ultraviolet spectra of the product (=CH 3.3 μ, >C=O 5.8 μ, C=C 6.2 μ, λ_{max} 298 mμ, ε 101) were consistent with the structure of 1,3-dimethyl-3-ethylbicyclo[2.2.2]oct-5-en-2-one (III).

Anal. Calcd. for $C_{12}H_{18}O$: C, 80.85; H, 10.18. Found: C, 80.79; H, 10.36.

Pyrolysis of III at 600° (1 mm.) afforded 2,6-dimethylphenol, m.p. 41–43° after recrystallization, identified by analysis and by a comparison of its infrared and ultraviolet spectra (λ_{max} 278, 272 mμ, ε 1647, 1562) with those of an authentic sample of 2,6-dimethylphenol; m.p. 44–45°, λ_{max} 278, 272 mμ, ε 1610, 1549.

Reaction of ethylene with o-cresol. o-Cresol (80 g., two runs) and ethylene at 275° and 2600–3000 atm. for 13.5 hr. gave 57 g. (*ca.* 40% conversion) of ketone product boiling at 57–71° (0.4 mm.). Distillation gave 45 ml. boiling at 75° (1 mm.); n^{25}_{D} 1.4850; d_{25} 0.9723.

Anal. Calcd. for $C_{13}H_{20}O$: C, 81.20; H, 10.48. Found: C, 81.37; H, 10.69.

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[9] These phenols were identified as products obtained by the reaction of phenol with ethylene at 250° but their relative amounts were not determined.

[10] K. von Auwers and W. Mauss, *Ann.*, **460**, 240 (1928).

The infrared and ultraviolet spectra (=CH 3.25 μ, >C=O 5.8 μ, strained C=C 6.15 μ; λ_{max} 299 mμ, ε 99) were consistent with the alternative structures 1,3-diethyl-3-methylbicyclo[2.2.2]oct-5-en-2-one (V) or the position isomer 3,3-diethyl-1-methylbicyclo[2.2.2]oct-5-en-2-one (VI). The ketone V (or VI) failed to give a derivative with 2,4-dinitrophenylhydrazine.

The remainder of the distillate (13 ml.; b.p. 52–74° (1 mm.)) afforded with 2,4-dinitrophenylhydrazine the dinitrophenylhydrazone of 3-methyl-3-ethylbicyclo[2.2.2]oct-5-en-2-one (IV); m.p. 146–148°. After several recrystallizations from ethanol it melted at 154.5–155.5°.

Anal. Calcd. for $C_{17}H_{20}O_4N_4$: C, 59.29; H, 5.85; N, 16.27. Found: C, 58.98; H, 5.98; N, 16.44.

Characterization of the products from resorcinol. The product from the reaction of resorcinol (100 g., two runs) with ethylene at 250° and 2700–3000 atm. for 14.5 hr. was freed of grease and phenolic material. Distillation gave 138 g. (55% conversion) of light yellow liquid of the composition $C_{16}H_{26}O_2$; b.p. 76–100° (0.1 mm.); n_D^{25} 1.4871. This was combined with a previous product (b.p. 71–102° (0.1 mm.); n_D^{25} 1.4871–1.4933) to make a total of 180 g. which was fractionally distilled. After a forerun of 10 ml. (b.p. 74–97° (0.5 mm.)), 80 ml. of 1,1,3,3,5-pentaethyl-4-cyclohexen-2,6-dione (VII) was obtained; b.p. 97–98° (0.5 mm.); n_D^{25} 1.4849.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.80; H, 10.34.

The presence of conjugated and unconjugated carbonyl groups in the cyclohexenedione (VII) was apparent from the infrared (5.85 μ, 6.0 μ) and ultraviolet spectra λ_{max} (shoulder) 315 mμ, ε 75, λ_{max} 231 mμ, ε 8400. The nmr spectrum of the compound indicated the presence of olefinic hydrogen. Since the compound contained a conjugated carbonyl group, the possibility of a bicyclic system was eliminated. In view of the structure of the products from phenol, it seemed unlikely that alkylation *beta* to the hydroxyl groups would occur to any appreciable extent. Thus, the five ethyl groups were assigned the remaining three possible positions to give proposed structure VII.

Distillation did not effect the separation of the remaining two components (VIII and IX); however, the last material collected (40 ml., b.p. 106–111° (0.5 mm.); n_D^{25} 1.4928–1.4935) was free of the cyclohexendione, as shown by the absence of a 6.0 μ carbonyl band in the infrared spectrum of this fraction and also by the ultraviolet spectrum, λ_{max} 300 mμ, ε 120.

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.70; H, 10.49.

In another experiment, a total boiling range of 85–125° (0.5 mm.) (n_D^{25} 1.4831–1.4952) was observed during fractionation of a similar resorcinol/ethylene product. A constant boiling fraction (b.p. 120° (0.5 mm.); n_D^{25} 1.4931) containing ketones VIII and IX was obtained.

Evidence for the presence of compounds VIII and IX ($C_{16}H_{26}O_2$) in the higher boiling fraction resides in the appearance of a hydroxyl band (2.8 μ) of moderate intensity and two unconjugated carbonyl bands (5.8 μ, 5.85 μ) in the infrared spectrum. That the hydroxyl was of the alcohol type (non-phenolic) was evidenced by the lack of absorption due to hydrogen bonding in this region of the spectrum and the absence of aromatic absorption in the 6–7 μ region. Accordingly, the diketone and isomeric hydroxy ketone structures VIII and IX are proposed.

Characterization of the products from hydroquinone. The product from the reaction of 275 g. of hydroquinone (five runs) and ethylene at 250° and 3000 atm. was distilled under reduced pressure. The distillate was dissolved in pentane, and the solution was extracted with five 200-ml. portions of Claisen's alkali. After the solution was dried over anhydrous calcium sulfate, the solvent was removed. Distillation of the residue afforded 352 g. (55%) of yellow oil, n_D^{25} 1.4885. This product was redistilled in a 13 mm.-diameter Podbielniak column.

TABLE I

DISTILLATION OF HYDROQUINONE-ETHYLENE PRODUCT

Fraction	Vol., ml.	B.P., °/20 mm.	n_D^{25}
1	10	93–149	1.4488
2–5	30	150–161	1.4871–1.4885
6–7	20	161–162	1.4899
8	5	162–163	1.4880
9–10	20	163	1.4909
11–13	41	163–164	1.4900–1.4886
14	6	164–172	1.4843
15	60	172–175	1.4894
16	15	175–185	1.4935
17–18	30	185–188	1.4922
19	15	188–189	1.4930
20–21	21	189–195	1.4937
22	4	195	1.4923
23–25	25	195–196	1.4955

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: Fraction 6–7: C, 76.59; H, 10.22. Fraction 9–10: C, 76.98; H, 10.12. Fraction 17–18: C, 76.92; H, 10.34. Fraction 20–21: C, 76.90; H, 10.32.

Calcd. for $C_{18}H_{30}O_2$: C, 77.65; H, 10.86. Found: Fraction 23–25: C, 77.47; H, 10.77.

Fractions 6–7 and 9–10 showed intense conjugated carbonyl absorption in the infrared at 5.95 μ with weaker unconjugated carbonyl absorption at 5.8 μ, and they absorbed in the ultraviolet at λ_{max} 253, 365 mμ, ε 10,000, 65. The infrared spectra of subsequent fractions indicated the presence of the same major component through fraction 11–13. Thus, these fractions appeared to contain conjugated ketone of the type X with lesser amounts of bicyclic ketone XI. The infrared spectrum of fraction 15 showed a preponderance of ketone with absorption at 5.8 μ and the presence of a much lesser amount of conjugated ketone (5.95 μ). Fraction 17–18 contained an even greater preponderance of unconjugated ketone which appeared to be an isomer of the main component of fraction 15 since other infrared absorption bands did not correspond (λ_{max} (inflection) 365 mμ, ε 8.75; λ_{max} (shoulder) 300 mμ, ε 75; λ_{max} 253, ε 1275). Fraction 20 also was comprised largely of unconjugated ketone. Intense absorption was noted at 11.95 μ in the infrared spectra of fractions 15–20 which was entirely lacking in fraction 23–25 even though this fraction showed intense carbonyl absorption at 5.8 μ with only a weak shoulder at 5.95 μ (λ_{max} 293, 251 mμ, ε 222, 1029).

Fraction 17–18 solidified to white crystals, m.p. 49–55°. Several recrystallizations from pentane at low temperature raised the melting point to 59–60° (>C=O 5.8 μ; λ_{max} 298 mμ, ε 50).

Anal. Calcd. for $C_{16}H_{26}O_2$: C, 76.75; H, 10.47. Found: C, 76.77; H, 10.52.

On this basis fractions 15–20 appear to be predominantly a mixture of isomeric bicyclic $C_{16}H_{26}O_2$ ketones (XI). The simplicity of the infrared spectrum of fraction 23–25 and the absence of the 11.95 μ band together with the ultraviolet spectrum indicate that this material is not bicyclic and contains a minor amount of conjugated ketone.

Reaction of catechol with ethylene. The reaction of 120 g. of catechol (three runs) with ethylene at 250° and 3000 atm. for 13–16 hr. afforded 253 g. of yellow viscous oil. The product was triturated with pentane and filtered. After the removal of phenolic material by extraction of the pentane solution with Claisen's alkali, the dried solution was distilled to obtain 59 g. (37% conversion) of yellow oil, b.p. 84–110° (0.6 mm.), n_D^{25} 1.4976. This material was combined with a previous product obtained in the same manner (n_D^{25} 1.4972) to make a total of 104 g. of material for fractionation. Distillation in a 30" column afforded a large, constant boiling fraction (52 ml., b.p. 86° (0.4 mm.), n_D^{25} 1.4980) apparently derived from the combination of catechol with four moles of ethylene.

Anal. Calcd. for $C_{14}H_{22}O_2$: C, 75.63; H, 9.97. Found: C, 75.71; H, 9.95.

The infrared and ultraviolet spectra of this fraction, however, showed that it was a mixture; —OH 2.9 μ (nonphenolic), >C=O 5.8, 6.0 μ, C=C 6.1 μ (shoulder), λ_{max} 303, 239 mμ, ε 80, 5800.

Characterization of products from phenol and propylene. The product from the reaction of 80 g. of phenol (two runs) with propylene at 275° and 3000 atm. was dissolved in pentane and extracted with several portions of Claisen's alkali. The product (22 g.) obtained by distillation of the dried pentane solution appeared to consist of aromatic ether and nonaromatic hydrocarbon on the basis of its infrared spectrum. Distillation of the phenols obtained by acidification and extraction of the Claisen's alkali solution afforded (a) 11 g., b.p. 110–120° (17 mm.), n_D^{25} 1.5153; (b) 103 g. (65% conversion) of crude 2,6-diisopropylphenol, b.p. 120–126° (17 mm.) together with fractions b.p. 55–67° (0.2 mm.), n_D^{25} 1.5124–1.5063; and (c) a residue of 5 g. The analysis and the ultraviolet spectrum of a constant boiling fraction obtained in the above distillation were consistent with the values for 2,6-diisopropylphenol, 38 g., b.p. 126° (17 mm.), n_D^{25} 1.5111, λ_{max} 278, 271 mμ, ε 1890, 1870. Since the last cut obtained in the distillation had a very similar ultraviolet spectrum (λ_{max} 278, 271 mμ, ε 1744, 1707), it appears that the crude 2,6-diisopropylphenol was contaminated with a small amount of hydrocarbon.

Characterization of the products from phenol and isobutylene. The product from the reaction of phenol (120 g., three runs) and isobutylene at 275° and 3000 atm. for 14 hr., was dissolved in pentane and extracted with three 200-ml. portions of Claisen's alkali. After the pentane was removed from the dried solution, the residue (105 g.) was distilled to obtain 68 g. (28% conversion) of 2,6-di-*t*-butylphenol, b.p. 136–143° (21 mm.), n_D^{25} 1.4989–1.5001. The refractive index and infrared spectra of the lower (n_D^{25} 1.4719) and higher boiling fractions (n_D^{25} 1.48–1.46) indicated that these materials were largely hydrocarbons. The crude 2,6-di-*t*-butylphenol was redistilled in a 36″ column to obtain 51 ml. of pure 2,6-di-*t*-butylphenol, b.p. 133° (20 mm.), m.p. 34–37°, λ_{max} 278, 271 mμ, ε 1750, 1730.

Acidification and extraction of the Claisen's alkali solution afforded 55 g. (29% conversion) of 2-*t*-butylphenol, b.p. 96–107° (16 mm.), n_D^{25} 1.5211. Redistillation gave 37 g. of pure 2-*t*-butylphenol, b.p. 101–103.5° (13 mm.), n_D^{25} 1.5212, λ_{max} 278, 271 mμ, ε 2070, 2025, having the correct analysis.

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[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Some Applications of Isopropylidene Malonate and Its Derivatives to the Synthesis of Cyclic Compounds

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Diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate and its 3-methyl and 3-phenyl derivatives have been prepared by treating the sodium salts of diisopropylidene methylenedimalonate, diisopropylidene ethylidenedimalonate, and diisopropylidene benzylidenedimalonate, respectively, with iodine or bromine. By alkylation of the sodium salt of isopropylidene malonate in dimethylformamide at room temperature, isopropylidene 1,1-cyclohexanedicarboxylate and isopropylidene 1,1-cyclopentanedicarboxylate have been prepared.

Methylations of isopropylidene malonate (I) have yielded principally the dimethylmalonate derivative. The reactions have been carried out by treating the isolated silver salt, in ether suspension, with methyl iodide,[3] or, better, by treating isopropylidene malonate with silver oxide and methyl iodide in acetonitrile.[4] It has now been found that benzylation of this malonic acid derivative likewise has a strong tendency to proceed to the dialkylation product. Alkylation with benzyl chloride in methanol, ethanol or dimethylformamide (DMF) gave only isopropylidene dibenzylmalonate, as did also a reaction of the sodium salt of isopropylidene malonate with benzyldimethylphenylammonium chloride. Isopropylidene benzylmalonate was obtained by hydrogenation of the benzalmalonate.[5]

These observations suggested that the alkylation of isopropylidene malonate with methylene iodide be examined. The various products that might be expected from reaction between these reagents are diisopropylidene methylenedimalonate (IIa),[5] the cyclobutane derivative (IV) and isopropylidene methylenemalonate (V). When the reaction was carried out in acetonitrile with approximately equimolar quantities of the dihalide, the malonate and silver oxide, a product was obtained which proved to be none of these. The infrared spectrum of the substance was identical with that of a compound obtained earlier from diisopropylidene ethylenetetracarboxylate (VI)[6] and diazomethane, and the identity of the two samples was confirmed by a mixed melting point determination. Mild hydrolysis converted the compound to 1,1,2,2-cyclopropanetetracarboxylic acid. Thus the reaction product must be diisopropylidene 1,1,2,2-cyclopropanetetracarboxylate (IIIa).

The cyclopropane derivative (IIIa) was probably

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