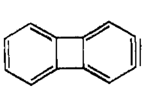
Communications

See Editorial, *J. Org. Chem.*, **37**, No. 13, 4A (1972).

2,3-Dehydrobiphenylene

Summary: Thermal decomposition of 2-biphenylenediazonium 3-carboxylate affords 2,3-dehydrobiphenylene which forms 2-chlorobiphenylene with 1,2-dichloroethane, biphenylenebicyclo[2.2.2]octatriene with benzene, and 1,2,3,4-tetraphenylbenzo[*b*]biphenylene with tetraphenylcyclopentadienone.

Sir: As part of our program to synthesize the higher homologs of biphenylene which incorporate four-membered rings into an annellated system, we have been able to generate and trap the novel aryne, 2,3-dehydrobiphenylene (**1**). The precursor[1] of **1**, 2-biphenylenediazonium 3-carboxylate (**2**), was prepared starting with 2-acetamido-3-bromobiphenylene[2] which on treatment with cuprous cyanide in dimethylformamide gave 2-acetamido-3-cyanobiphenylene. Hydrolysis of the cyano group with hot concentrated hydrochloric acid afforded 2-acetamidobiphenylene-3-carboxylic acid which on treatment with sodium hydroxide in aqueous ethanol gave 2-aminobiphenylene-3-carboxylic acid (**3**). Diazotization of **3** with isoamyl nitrite in tetrahydrofuran containing a trace of trichloroacetic acid gave **2**. Thermal decomposition of **2** in the presence of tetraphenylcyclopentadienone yielded the adduct **4** isolated *via* chromatography (neutral alumina–pentane) in 10% yield: white needles; mp 316–317.5°; uv max (cyclohexane) 251 nm (ϵ 27,500), 274 (50,700), 282 (66,700), 296 (42,800), 309 (55,100), 341 (7250), 353 (5070), 373 (6520), 394 (6520); nmr ($CDCl_3$) δ 7.15 (s, 10, C-1 and C-4 phenyls), 6.80 (s) and 6.76 (s) (16, C-2 and C-3 phenyls + biphenylene); mass spectrum *m/e* 506 (parent).



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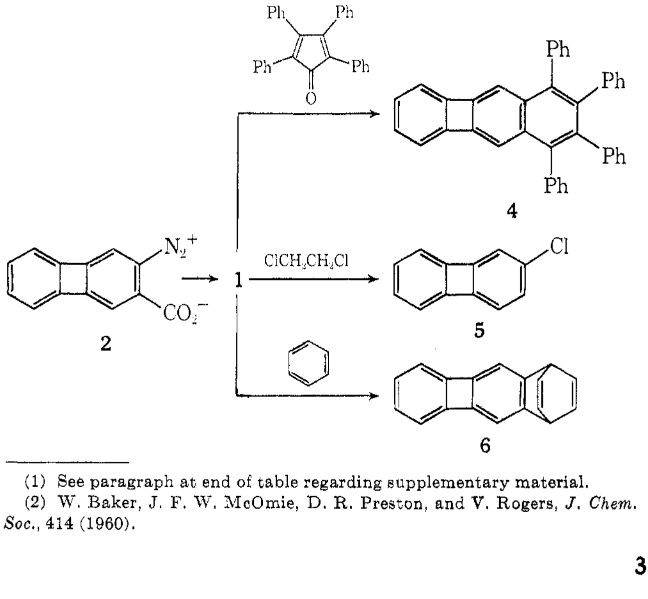

Attempts to isolate the dimer of **1** have thus far been unsuccessful. Thus, the thermal decomposition of **2** in refluxing 1,2-dichloroethane affords as the main product (9% yield) 2-chlorobiphenylene **5**.[3] In refluxing benzene **2** affords mostly polymeric material accompanied by a small amount (1%) of biphenylenebicyclo[2.2.2]octatriene (**6**): a yellow solid; mp 156–158°; nmr ($CDCl_3$) δ 7.2–6.3 (m, 10, aromatic plus olefinic), 5.0–4.7 (m, 2, bridgehead); mass spectrum *m/e* 228 (parent) 202 (P − C_2H_2).

Attempts at crossing 2,3-dehydrobiphenylene with benzyne resulted primarily in the independent dimerization of benzyne to yield biphenylene.

It is evident from the trapping experiments that 2,3-dehydrobiphenylene generated from the diazonium carboxylate **2** is a true aryne, undergoing cycloaddition reactions typical of the highly reactive intermediates. However, under conditions generally favorable for aryne dimerization, **1** either does not undergo aryne coupling (*i.e.*, dimerization or crossing) or does so in such a myriad of concomitant reactions that the expected products are not isolable.

Regardless of this, 2,3-dehydrobiphenylene is in itself an interesting intermediate warranting further synthetic and theoretical investigation.[4]

Supplementary Material Available.—Details of the syntheses of the compounds reported here along with spectral information will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20 × reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number JOC-1973-3812.

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(1) See paragraph at end of table regarding supplementary material.

(2) W. Baker, J. F. W. McOmie, D. R. Preston, and V. Rogers, *J. Chem. Soc.*, 414 (1960).

(3) W. Baker, J. W. Barton, and J. F. W. McOmie, *J. Chem. Soc.*, 2666 (1958).

(4) This investigation was assisted financially by a grant from the National Science Foundation.

(5) Taken in part from the thesis of E. N. Losey, submitted in partial fulfillment of the requirement for the Ph.D. degree at Michigan State University, 1973.

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Three-Electron Oxidations. V. The Rapid Reaction of Chromic Acid with Two-Component Substrate System[1,2]

Summary: The chromic acid oxidation of binary systems containing isopropyl alcohol and bifunctional compounds such as dicarboxylic acids, hydroxy acids, and aldehydo or keto acids can be much faster than

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(1) Part IV: F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **95**, 5421 (1973).

(2) This investigation was supported by the National Science Foundation.

that of either of the two substrates; hydroxy acids and picolinic acid are most effective in accelerating the oxidation.

Sir: We have recently reported[3] a dramatic rate acceleration of two to three orders of magnitude observed in the chromic acid oxidation of a two-substrate system of isopropyl alcohol and oxalic acid. The results lead us to propose a mechanism consisting of the formation of a termolecular complex and its decomposition in a single-step three-electron oxidation reaction.

We now wish to report that the ability to accelerate the chromic acid oxidation of isopropyl alcohol is not restricted to oxalic acid, but is shared by a large number of other substrates, particularly by those which could be expected to form relatively stable (usually bidentate) complexes with chromic acid.

The results are summarized in Table I. The first column shows the experimental pseudo-first-order rate constant for the oxidation of the given substrate in the absence of isopropyl alcohol. The next gives the sum of this value and of the pseudo-first-order rate constant for the oxidation of isopropyl alcohol and represents the oxidation rate for the mixture of the two substrates in the absence of any rate acceleration. The next column gives the observed oxidation rate for the mixture of isopropyl alcohol and the substrate. With the exception of succinic acid, ethylene glycol, and diethylene glycol the observed rate constant is always higher than that calculated in the preceding column. The last two columns represent two different quantitative measures of the rate accelerating effect. Column five gives the ratio of the observed to the calculated rate constant. The last column gives a rate constant computed on the assumption that a third-order term (first order in the substrate, in isopropyl alcohol, and in chromic acid) is responsible for the observed rate acceleration.[3]

TABLE I

EFFECTIVENESS OF SOME SUBSTRATES IN COOXIDATION REACTIONS WITH CHROMIC ACID AND ISOPROPYL ALCOHOL[a]

Substrate (*M*)	10^3k, sec^{-1}	$10^3\Sigma k$,[b] sec^{-1}	10^3k_{obsd}, sec^{-1}	$\frac{k_{obsd}}{\Sigma k}$	$\frac{10^3(k_{obsd} - \Sigma k)}{[\text{substrate}][i\text{-PrOH}]}$
$(COOH)_2$ (0.254)	51.3	52.5	151	2.9	9940
$CH_2(COOH)_2$ (0.101)	0.126	1.29	1.31	1.02	6.09
$MeCH(COOH)_2$ (0.268)	0.277	1.44	1.61	1.12	16.6
$Me_2C(COOH)_2$ (0.203)	0.0009	1.16	1.41	1.22	31.6
$EtCH(COOH)_2$ (0.363)	0.231	1.39	1.61	1.15	15.5
$Et_2C(COOH)_2$ (0.179)	0.009	1.17	1.39	1.18	31.5
$(CH_2)_2(COOH)_2$ (0.158)	0.0022	1.16	1.16	1.00	0
$MeCH{=}CHCOOH$ (0.191)	0.126	1.29	1.51	1.17	30.1
Fumaric acid (0.076)	0.120	1.28	1.61	1.26	111
Maleic acid (0.189)	0.533	1.69	2.57	1.52	119
Citraconic acid (0.231)	1.98	3.14	3.65	1.16	56.6
Mesaconic acid (0.073)	0.478	1.64	1.93	1.17	103
$O(CH_2COOH)_2$ (0.241)	0.026	1.19	1.65	1.38	48.9
$HOCH_2CO_2H$ (0.237)	1.73	2.89	6.93	2.40	437
$MeCH(OH)COOH$ (0.134)	10.8	12.0	13.9	1.16	360
$Me_2C(OH)COOH$ (0.156)	0.116	1.28	5.78	4.52	740
$MeEtC(OH)COOH$ (0.170)	0.165	1.33	8.25	6.20	1040
Malic acid (0.267)	4.47	5.63	13.3	2.36	737
meso-Tartaric acid (0.205)	10.8	12.0	69.3	5.78	7170
d-Tartaric acid (0.198)	11.6	12.8	46.4	3.63	4370
Citric acid (0.232)	0.087	1.25	9.60	7.68	923
$OCHCOOH$ (0.065)	96.2	97.4	116	1.19	733
$EtCOCOOH$ (0.173)	131	132	151	1.14	282
$HOOCCH_2CH_2COCOOH$ (0.232)	21.0	22.2	31.5	1.42	1030
$HOOCC(OH)_2C(OH)_2COOH$ (0.034)	7.22	8.38	28.9	3.45	15460
$HOCH_2CH_2OH$ (0.359)	2.89	4.05	4.08	1.01	2.14
$(HOCH_2CH_2)_2O$ (0.191)	1.24	2.40	2.41	1.00	1.34
$H_2NCH_2CO_2H$ (0.687)	0.0071	0.0187[c]	0.0201[c]	1.07[c]	5[c]
		1.17	1.31	1.12	5
Picolinic acid (0.264)	0.116	0.232[d]	8.06[d]	35[d]	7600[d]
		1.27	119	93	11800

[a] $t = 60°$, $HClO_4$ 0.628 *M*, *i*-PrOH 0.039 *M*, $k_{i\text{-PrOH}} = 1.16 \times 10^{-3}$ sec^{-1}. [b] $\Sigma k = k_{substrate} + k_{i\text{-PrOH}}$. [c] [*i*-PrOH] = 3.9×10^{-4} *M*. [d] [*i*-PrOH] = 3.9×10^{-3} *M*.

Among the group of simple dicarboxylic acids, the previously investigated oxalic acid is by far the most effective participant in cooxidation reactions. Succinic acid is entirely unreactive. Malonic acid shows only a small rate-accelerating effect, whereas mono- and, particularly, dialkylmalonic acids are much more effective. This trend would be expected if the observed acceleration was due to a three-electron oxidation leading to $\cdot CH_2CO_2^-$, $R\dot{C}HCO_2^-$, and $R_2\dot{C}CO_2^-$, respectively, in analogy to the mechanism proposed for the cooxidation of oxalic acid.[3] In fact, the acceleration for disubstituted malonic acids is quite impressive considering the very low oxidation rates of these acids in the absence of the alcohol.

While we anticipated the possible rate-acclerating effect for maleic acid, the observed rate acceleration for fumaric acid and particularly for crotonic acid was entirely unexpected.

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(3) F. Hasan and J. Roček, *J. Amer. Chem. Soc.*, **94**, 3181 (1972).

One of the most interesting classes of compounds included in Table I are the hydroxy acids which proved extremely effective in accelerating the oxidation of isopropyl alcohol. Aldehydo acids, keto acids, and diglycolic acid (containing an ether function) show less impressive but still quite substantial rate accelerations.

Another very high rate acceleration was observed for picolinic acid. The change in the value in the last column indicates that the reaction probably follows a different rate law than observed previously for oxalic acid.[3] Glycine affects the rate of the oxidation of isopropyl alcohol only to a very small extent.

Detailed investigations of several of the reactions reported in this communication are in progress.

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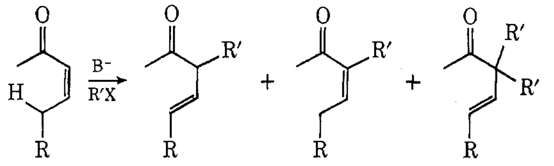
Regioselective Methylations of 2-Thioalkoxyenones

Summary: Methylation (methyl iodide) of the kinetic enolate generated from 2-thio-*n*-propyl-5,5-dimethyl-2-cyclohexen-1-one and lithium hexamethyldisilazide in tetrahydrofuran takes place at C_6, whereas methylation of the potassium enolate in *tert*-butyl alcohol occurs at C_2.

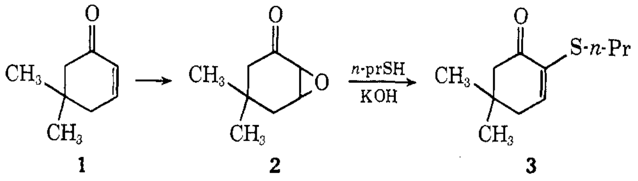
Sir: Alkylation of an α,β-unsaturated ketone having γ-hydrogen atoms under enolate equilibrating conditions usually results in formation of an α-alkyl-β,γ-unsaturated ketone (Scheme I). A major problem, however, is that this initial product may be isomerized to an α-alkyl-α,β-unsaturated ketone or may undergo further alkylation.[1] This problem could not arise during alkylation of 2-thioalkoxyenones, in which the enone α-hydrogen atom is replaced by a potentially removable thioalkoxy group (*e.g.*, **3**).

SCHEME I

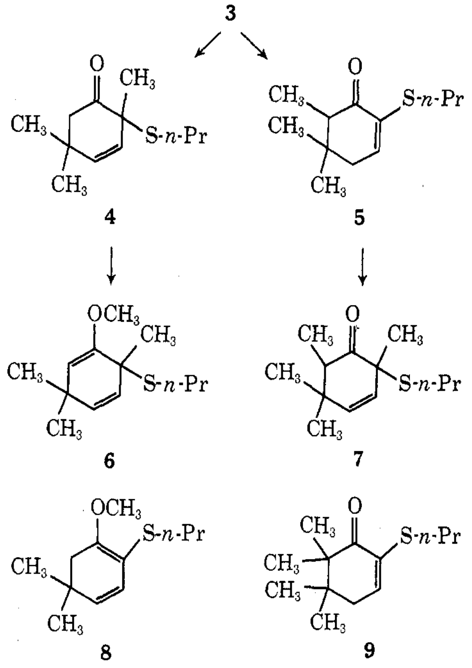


We wish to report some preliminary alkylation studies of thioalkoxyenones, here represented by 2-thio-*n*-propyl-5,5-dimethyl-2-cyclohexen-1-one (**3**). By simply varying the reaction conditions, we have been able to effect nearly quantitative carbon alkylation at either the 2 position in **3** to give enone **4** or at the 6 position to give enone **5** (Scheme III).

SCHEME II



SCHEME III



Cyclic 2-thioalkoxyenones may be efficiently prepared from the corresponding enone *via* an epoxy ketone.[2] In the present case (Scheme II), potassium hydroxide catalyzed reaction of epoxide **2**[3] with *n*-propyl mercaptan in ethanol gave 2-thioalkoxycyclohexenone **3** in 94% isolated yield [bp 94–96° (~0.3 Torr), *m/e* 198].

Methylation of the potassium enolate of **3** generated by addition of **3** (10 g) to a solution of 1.1 equiv of potassium *tert*-butoxide in dry *tert*-butyl alcohol followed by addition of 2 equiv of methyl iodide gave predominately the 2-alkylated enone **4** (95%), some dialkylated enone **7** (4%), and a trace of enol ether **6** (Scheme III).[4] Enone **4** [80% isolated yield, bp 90° (~0.4 Torr), *m/e* 212] displayed olefinic proton resonance centered at δ 5.43 and 5.72 (J_{AB} = 10 Hz) and ir absorption at 5.87 μ (film).

It is noteworthy that oxygen alkylation of **3** to give **8** did not occur under these conditions. Indeed, even when the potassium enolate[5] of **3** was methylated in tetrahydrofuran (THF) solution (conditions known to facilitate oxygen alkylation), no oxygen alkylation of **3** could be detected. Under these conditions, **4** (75% yield), **5** (14%), **6** (6%), and recovered **3** (3%) were obtained. This result is to be contrasted with methylation of the potassium enolate of ketone **4** in THF–hexamethylphosphoramide (HMPA) solution to give predominately oxygen-alkylated **6** (90%), along with **7** (10%).

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(1) H. O. House, "Modern Synthetic Reactions," 2nd ed, W. A. Benjamin, Menlo Park, Calif., 1972, Chapter 9.

(2) M. A. Tobias, J. G. Strong, and R. P. Napier, *J. Org. Chem.*, **35**, 1709 (1970).

(3) R. L. Wasson and H. O. House, *Org. Syn.*, **37**, 58 (1957).

(4) An F & M Model 700 gas chromatograph fitted with a thermal conductivity detector and a 6 ft × $1/8$ in. stainless steel column filled with 10% UC-W98 on Chromosorb W, 80–100 mesh size, at 170° was used.

(5) Generated by addition of **3** to a suspension of potassium hydride in THF. This base-solvent combination has been used to generate ketone enolates in their equilibrium ratios: C. A. Brown, private communication; C. A. Brown, *J. Amer. Chem. Soc.*, **95**, 982 (1973).