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A NEW METHOD FOR THE SYNTHESIS OF BUTATRIENES

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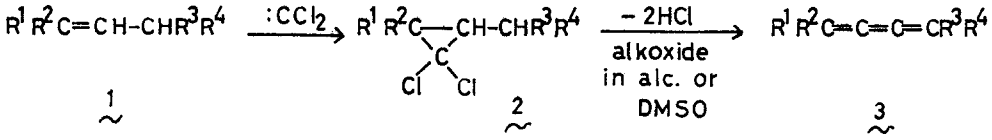
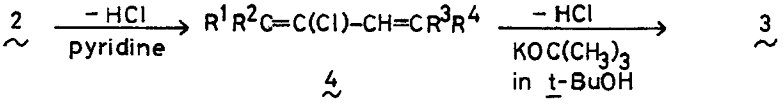
Methods for synthesizing butatrienes are not numerous$^{1)}$. A technique of reduction of butynediols is known as an usual synthetic method for butatrienes, but the yields of butatrienes by this method are generally low. We wish to report a new method for the synthesis of butatrienes.

Reaction of olefins 1 with dichlorocarbene gave gem-dichlorocyclopropanes 2. The dichlorocarbene was generated from the reaction of ethyl trichloroacetate with sodium methoxide$^{2)}$, or chloroform with aqueous sodium hydroxide solution (50 %) in the presence of catalytic amounts of benzyltriethylammonium chloride$^{3)}$. Butatrienes 3 were immediately derived from 2 by the ring opening reaction of 2 with alkoxides (potassium t-butoxide in t-butyl alcohol, sodium methoxide in dimethyl sulfoxide, or sodium ethoxide in dimethyl sulfoxide) in satisfactory yields (see Table).



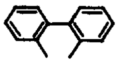
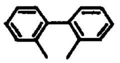
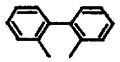
When hot pyridine was used as a base and a solvent instead of alkoxides in alcohols, 2-chlorobuta-1,3-diene derivatives 4 were obtained in good



$$\underset{\sim}{2} \xrightarrow[\text{pyridine}]{-\text{HCl}} \underset{\underset{\sim}{4}}{R^1R^2C{=}C(Cl){-}CH{=}CR^3R^4} \xrightarrow[\substack{KOC(CH_3)_3 \\ \text{in } \underline{t}\text{-BuOH}}]{-\text{HCl}} \underset{\sim}{3}$$

yields. The compounds **4** were easily converted into **3** by refluxing with potassium *t*-butoxide in *t*-butyl alcohol. Consequently, it is apparent that the reaction of **2** with alkoxides led to **3** via intermediates **4**.

A typical procedure is as follows. To a solution of potassium *t*-butoxide in *t*-butyl alcohol (potassium 0.12 g, 0.003 g-atom; *t*-butyl alcohol 50 ml) was added 0.43 g (0.001 mole) of 2,2-biphenylene-1,1-dichloro-3-(9-fluorenyl)-cyclopropane, which was prepared from the reaction of 1,1-biphenylene-3,3-biphenylene-1-propene4) with dichlorocarbene by method of Makosza et al3) in 46% yield. The mixture was refluxed for 30 min to afford dark red crystals 3c7): 0.32 g (91 %); mp 306°C (from dioxane).

	R^1	R^2	R^3 8)	R^4	Color	Mp(°C)	Spectra	Yield(%)
3a5)	C_6H_5	C_6H_5	C_6H_5	C_6H_5	yellow	234	λ_{max} 424 mμ	73
3b6)			C_6H_5	C_6H_5	orange	223-4	λ_{max} 458 mμ ν_{max} 2050 cm^{-1}	97
3c7)					dark red	306	λ_{max} 484 mμ	91
3d	CH_3O	C_6H_5	C_6H_5	C_6H_5	orange red	129-131	λ_{max} 406 mμ ν_{max} 2045 cm^{-1}	78
3e	CH_3O	C_6H_5	p-CH_3O-C_6H_4	C_6H_5	"	oil	ν_{max} 2040 cm^{-1}	44
3f	CH_3O	C_6H_5	p-CH_3-C_6H_4	C_6H_5	"	"	ν_{max} 2040 cm^{-1}	50

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8. When CH_3 group was chosen as R^3 , enyne derivatives R^1R^2CH-$C{\equiv}C$-$CR^4{=}CH_2$ and allene derivatives $R^1R^2C{=}C{=}CH$-$CR^4{=}CH_2$ were obtained.