Instability of the Butenylcadmium Reagent

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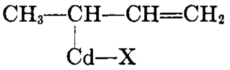
Although organocadmium reagents have found wide application for synthesis of ketones,[2] the only alkyl radicals which may be utilized satisfactorily are primary ones. Secondary or tertiary alkylcadmium reagents are too unstable,[3] even at 0°, to allow their effective use in synthesis. It seems probable that the principal route[4] of decomposition of the cadmium reagent involves dissociation to free radicals which disproportionate to a mixture of alkane and alkene. Although it would be predicted that the crotylcadmium reagent would be more prone to dissociate than an *n*-alkylcadmium reagent, because of resonance stabilization of the radical containing an allylic structure, the allyl type of reagent might still prove sufficiently stable for use in synthesis provided its structure involves only the primary radical (I or the dialkenylcadmium structure) and no equilibration with the secondary structure (II). The nuclear magnetic resonance spectrum of allylmagnesium bromide[5] has been interpreted as indicating an equilibrium between forms with either terminal carbon attached to magnesium; however, the ultraviolet spectrum of the Grignard reagent from cinnamyl bromide[6] has a form suggesting the primary structure analogous to I.

$CH_3—CH═CH—CH_2—Cd—X$

I



$$CH_3—\underset{\displaystyle Cd—X}{CH}—CH═CH_2$$

II

Since work in this laboratory has been concerned with utilization of the cadmium reagents in synthesis,[7] the stability of the butenylcadmium reagent has been examined. When the butenyl Grignard reagent was treated in the normal manner for conversion to a cadmium reagent,[2] and the reaction product was then treated with decanoyl chloride, the only higher-boiling products of the reaction appeared to be condensation products from the acid chloride. A preparation was then examined immediately after reaction of the Grignard reagent with cadmium chloride. Treatment of the solution with water at this point yielded only coupling products of the butenyl radicals, and no butene; therefore, it must be concluded that the butenylcadmium reagent, if it is formed as such, rapidly dissociates at the temperature of boiling ether. Since the butenyl radical is relatively stable to disproportionation, coupling results.

Preparation of the butenyl Grignard reagent at high dilution[8] gave about 75% yield of reagent, as judged by titration, and about 25% yield of coupling products. The mixture of isomeric octadienes (III, IV, V) obtained as coupling products in

$CH_2═CHCH(CH_3)CH(CH_3)CH═CH_2$ III

$CH_3CH═CHCH_2CH(CH_3)CH═CH_2$ IV

$CH_3CH═CHCH_2CH_2CH═CHCH_3$ V

this preparation has been separated by distillation and characterized in work by Young, Roberts, and Wax.[9] Gas chromatographic analysis was used in the present work to obtain the ratio between isomers which is recorded in Table I. Although the ratio of isomers differs somewhat from that obtained previously by distillation, the order of abundance of isomers is the same (IV>V>III). After the Grignard reagent had been treated with cadmium chloride, there was obtained 78% yield of octadienes, and it is of interest that the ratio of

TABLE I

ISOMER DISTRIBUTION IN MIXTURES OF OCTADIENES[a]

	Distribution of Isomers,[b] %		
	III	IV	V
Coupling product after preparation of Grignard reagent	11	55	34
Coupling product after reaction with cadmium chloride[c]	10 14.5	50 49	40 36.5
Previously reported[d] from Grignard reagent	2	88	10

[a] Undistilled samples or unfractionated distillates were used for injection into an 8 mm. o.d. × 2 m. gas chromatography column containing as partitioning agent about 5% di-2-ethylhexyl phthalate on 30–60 mesh Celite firebrick. At a temperature of 53°, with helium flow of about 50 ml./min., retention times (from time of injection to maximum in peak) for isomers III, IV, and V were respectively 2:33 (min., sec.), 3:00 and 4:26. [b] Per cent of an isomer reported is the per cent of the area under all bands represented by the area under the band for that isomer. Bands were assigned on the basis of the boiling points previously reported,[9] i.e. the lowest-boiling isomer was assigned to the band of shortest retention time. In addition, one run was partially separated by fractional distillation (*cf.* Experimental). [c] Results given first are from the slow reaction with cadmium chloride in a dilute solution in ether, while those given second are in more concentrated solution (*cf.* Experimental). [d] See ref. 9.

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[2] J. Cason, *Chem. Revs.*, **40**, 15 (1947); D. A. Shirley, *Org. Reactions*, **Vol. 8**, John Wiley and Sons, Inc., New York, 1954, p. 28.

[3] J. Cason and F. S. Prout, *J. Am. Chem. Soc.*, **66**, 46 (1944).

[4] J. Cason, G. Sumrell, and R. S. Mitchell, *J. Org. Chem.*, **15**, 850 (1950).

[5] J. E. Nordlander and J. D. Roberts, *J. Am. Chem. Soc.*, **81**, 1769 (1959).

[6] R. H. DeWolfe, D. L. Hagmann, and W. G. Young, *J. Am. Chem. Soc.*, **79**, 4795 (1957).

[7] For the preceding report in this field, *cf.* J. Cason and R. J. Fessenden, *J. Org. Chem.*, **22**, 1326 (1957).

[8] W. G. Young, A. N. Prater, and S. Winstein, *J. Am. Chem. Soc.*, **55**, 4908 (1933).

[9] W. G. Young, J. D. Roberts, and H. Wax, *J. Am. Chem. Soc.*, **67**, 841 (1945).

isomers (*cf.* Table I) is in essential agreement with that obtained during preparation of the Grignard reagent. Thus, whatever mechanism is involved in the reaction of butenylmagnesium bromide with butenyl bromide, the factors controlling isomer distribution give results quite similar to those resulting from coupling of the butenyl radical.

EXPERIMENTAL[10]

Butenyl Grignard reagent was prepared according to the procedure of Young, Prater, and Winstein[8] from 1.5 moles of magnesium turnings and 0.5 mole of crotyl bromide.[11] There was used a total of 1 l. of anhydrous ether, and the bromide was added during about 4 hr.

Titration[12] of the solution of Grignard reagent indicated yields, in several runs, between 70 and 80%. In one run, the solution of Grignard reagent was concentrated by distillation of about 75% of the ether. Within the limits of experimental error (±10%), the assay by titration remained unchanged.

In a run in which the Grignard reagent was decomposed with water soon after it had been prepared, there was a violent reaction and evolution of large quantities of gas (not trapped). Work-up of the ether solution and distillation yielded 8.1 g. (25%) of a mixture of octadienes, b.p. 99–124°. This mixture was subjected to analysis by gas chromatography, with the results reported in Table I; no crotyl bromide was present. The infrared spectrum of the octadiene mixture exhibited absorption bands at the following wave lengths (μ): 3.32, 3.41 (doublet), 6.05, 6.82, 7.00, 7.25, 10.04, 10.32, 10.95.

Reaction of the butenyl Grignard reagent with cadmium chloride. A solution of Grignard reagent prepared as described above was transferred under nitrogen pressure to another flask in order to remove the large excess of magnesium. Assay of the transferred solution by titration was the same within experimental error (±3%) as before transfer. After there had been added over a 3-min. period 0.43 mole of anhydrous cadmium chloride, the mixture was stirred and heated under reflux until the Gilman test for Grignard reagent had become negative.[13] Titration[12] of the mixture after this period showed the presence of no material-consuming acid.

To the mixture was added 100 ml. of water, then the ether layer was separated, washed with water, and dried with magnesium sulfate. The bulk of the ether was removed by fractional distillation and the residue was subjected to analysis by gas chromatography (*cf.* Table I). Distillation[10] yielded a total of 21.7 g. (78%) of octadienes, b.p. 99–124°. This material was distributed in three main fractions: (1) b.p. 99–109°, n_D^{25} 1.4154–1.4209; (2) b.p. 110–114°, n_D^{25} 1.4233–1.4259; (3) b.p. 118–124°, n_D^{25} 1.4302–1.4309. For the isomeric octadienes (*cf.* formulas in text) there have been reported:[9] (III) b.p. 102°, n_D^{20} 1.4211; (IV) b.p. 111°, n_D^{20} 1.4240; (V) b.p. 124°, n_D^{20} 1.4336. Gas chromatography of the three fractions showed incomplete separation, as would be judged from the boiling point range; however, bands for only three components were observed, and the major band in each fraction was that expected from a correlation of retention time with boiling point.

The infrared spectrum of this mixture of octadienes was nearly identical with that exhibited by the mixture obtained directly from the preparation of Grignard reagent.

In one run, before cadmium chloride was added, a gas absorption line was arranged so that any exit gases would pass through two tubes of bromine thermostatted at 30° and then through a trap cooled in Dry Ice. Periodically, the flask and train were flushed with nitrogen. After the negative test for Grignard reagent had been obtained, the bromine was decomposed with sodium bisulfite; no water insoluble material was obtained. Also, no liquid was retained by the cold trap. A new absorbing train was put in place before water was added to the mixture. Again, no volatile gases were recovered.

In the run in which reaction with cadmium chloride was accelerated by concentration of the ether solution, results were essentially the same as when the dilute solution was utilized. Analysis of the octadiene mixture is included in Table I.

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[10] Boiling points are uncorrected; distillations were through a 65 cm. column of the simple Podbielniak design (*cf.* J. Cason and H. Rapoport, *Laboratory Text in Organic Chemistry*, Prentice-Hall, Inc., Englewood Cliffs, 1950, p. 237). Infrared spectra were recorded on a Baird spectrophotometer, using thin films.

[11] Gas chromatography of the "crotyl" bromide on silicone grease as partitioning agent indicated a composition of 11% methylallyl bromide and 89% crotyl bromide. Since the Grignard reagents from these two bromides have been found to be indistinguishable [*cf.* R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 735 (1956)], it was deemed not worthwhile to separate the minor content of methylallyl bromide.

[12] H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923).

[13] The cadmium reagent gives a negative result in this test [*cf.* H. Gilman and J. F. Nelson, *Rec. trav. chim.*, **55**, 518 (1936)]. In the dilute solution in which the Grignard reagent was prepared, about 12 hr. elapsed before the test was negative, but in a run in which the solution was concentrated to one-fourth volume the test became negative after about 30 min. under reflux. The slow reaction with cadmium chloride in dilute ether solution has been noted on several previous occasions in this laboratory.

Preparation and Spectra of Some Dinitroparaffins

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The only method reported in the literature for preparing α,ω-dinitroparaffins has been the classical Victor Meyer reaction in which the appropriate diiodoalkane was treated with silver nitrite in an ethereal solution.[2] A recent study has demonstrated, however, that this reaction is really useful only for the synthesis of primary nitroparaffins.[3] This note describes the preparation and spectra of a series of α,ω-dinitroparaffins and a comparable secondary dinitro compound.

The α,ω-dinitroparaffins can be successfully prepared by treating the appropriate dibromoalkane with sodium nitrite in *N,N*-dimethylformamide:

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[2] H. Feuer and G. Leston, *Org. Syntheses*, **34**, 37 (1954).

[3] N. Kornblum, B. Taub, and H. Ungnade, *J. Am. Chem. Soc.*, **76**, 3209 (1954); N. Kornblum, R. Smiley, H. Ungnade, A. White, and S. Herbert, *J. Am. Chem. Soc.*, **77**, 5528 (1955).