

METHYLENECYCLOPROPANE AS AN ALKENE COMPONENT
 IN THE KHAND-PAUSON REACTION

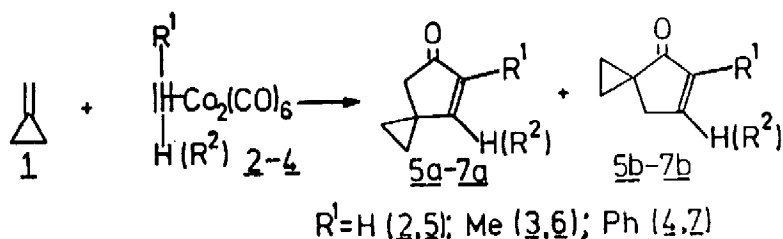
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Abstract: Interaction of methylenecyclopropane with dicobalthexacarbonyl complexes of various alkynes proceeds smoothly on the surface of solid supports and affords spiro[2.4]-heptenone derivatives in good yields.

Reaction of a dicobalthexacarbonyl complex (DCHCC) of an alkyne with an alkene leading to the formation of cyclopentenones ([2+2+1] cycloaddition, Khand-Pauson reaction¹) proceeds especially easily with the strained alkenes (e.g. norbornene or cyclobutene derivatives²). Since the reactivity associated with the strained nature of the double bond in methylenecyclopropane **1** is well documented in a variety of cycloadditions ([4+2], [3+2] or [2+2])³, it was surprising to find no reports regarding the use of **1** in [2+2+1] cycloadditions³. Here we present the results of our studies in this field.

Conventional conditions for the Khand-Pauson reaction involve the heating of the substrates in hydrocarbon solvents over a period of several hours (liquid phase conditions, LPC¹). When these conditions were tried for the reaction of **1** with the DCHCC of acetylene **2**, propyne **3**, or phenylacetylene **4**, the results turned out to be rather discouraging. Thus, a rapid consumption of the reagents was observed when a solution of **1** and **2** (or **3,4**) in hexane was kept at 20°C, but the reaction was accompanied by extensive tar formation and the respective cycloaddition products **5-7** were isolated in poor yields (10-15%, a:b ~ 1:1). Attempts to improve this procedure by variations in temperature, time, concentration or ratio of the components met with little success.

Scheme 1



Earlier we had shown that the intramolecular Khand-Pauson reaction could be run with an increased efficiency in a solvent-free system with the substrate applied to the surface of chromatography adsorbents (dry state adsorption conditions, DSAC⁴). However, a priori it seemed highly questionable that these DSAC could be used for an intermolecular Khand-Pauson reaction. Thus, it was both surprising and very rewarding to discover that under DSAC the [2+2+1] cycloaddition of **1** with **2-4** proceeded quite smoothly. In fact, heating the mixture of **1** with **3** (molar ratio 1:3 = 2:1) adsorbed on SiO₂ for 2 hours at 50° produced **6** in 64% yield (a:b ~ 5:1)^{5a}. Comparable results have been obtained when Al₂O₃ or MgOSiO₂ were used as "dry-media" for this reaction⁷ (see Table). Further studies

revealed that various zeolites may also be used as promoters for this reaction. While these promotion effects were shown to vary significantly, depending on the nature of the zeolites used, no useful correlations on the activity-structure dependence could be established (*vide infra*). A number of alkynes, both terminal and internal, were tested as substrates for [2+2+1] cycloaddition with **1** under DSAC on various supports. A set of representative results is given in Table (for the structures of the products, see Scheme 1⁹).

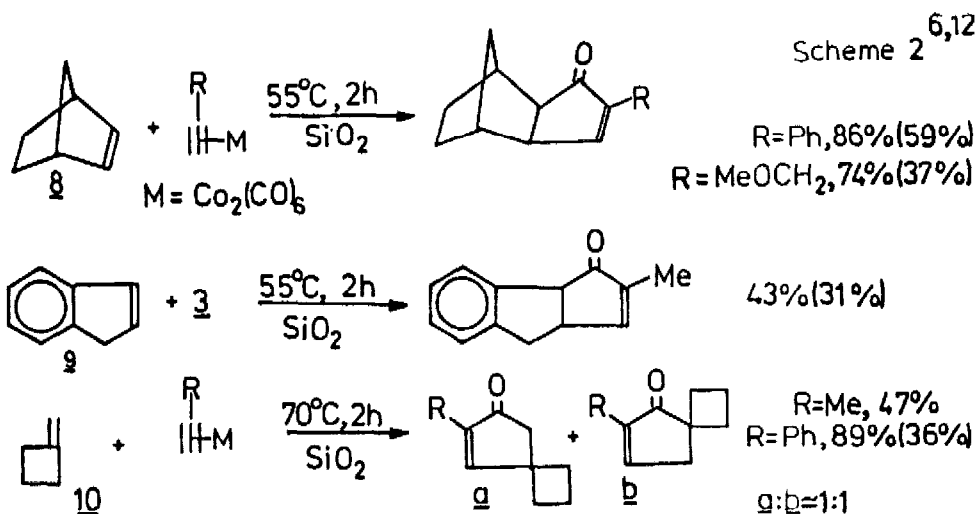
Entry	DCHCC of alkyne R ¹ , R ²	Conditions Support ⁹	T(°C)	τ (h)	Yield (%) ^{5,6,9}	Ratio a:b
1	H,H	SiO ₂	50	2	46	6:1
2	Me,H	SiO ₂	50	2	64	4.9:1
3	-"	Al ₂ O ₃	50	2	77	5:1
4	-"	MgOSiO ₂	50	0.5	53	2.5:1
5	-"	Zeolite NaX	50	2	81	2.3:1
6	Ph,H	SiO ₂	50	3	79	4.4:1
7	c-C ₃ H ₇ ,H	Zeolite NaX	50	1.5	67	3:1
8	CH ₂ =CH,H	-"	50	1	25	>20:1
9	CH ₂ =C(Me),H	-"	50	2	59	3:1
10	-"-"	Zeolite H-ZSM ¹⁰	50	0.5	69	5.5:1
11	MeOCH ₂ ,H	Zeolite NaX	50	1	79	5:1
12	Me ₂ C(OH),H	SiO ₂	50	6	47	3:1
13	Et,Et	Zeolite NaX	50	4	54	<1:20
14	Me ₃ Si,Me	-"	50	2	81	<1:20

Additional comments on these data seem to be appropriate: (i) The scope of the reaction is quite general and this reaction can be used for the preparation of various derivatives of spiro[2.4]heptenone including those containing functionalized substituents (entries 7-12); (ii) Cycloaddition proceeds with complete regioselectivity as regards the alkyne component producing 2-substituted derivatives from terminal alkynes (entries 1-12) and adducts containing the larger substituent at this position from internal alkynes (entry 14). (iii) Regioselectivity of the addition across the double bond of **1** for terminal alkynes may vary depending on the reaction conditions but in all cases the isomer containing spirosubstituents at the β -position is formed as a major component. On the contrary, α -spirosubstituted products are formed exclusively for the cycloadditions with internal alkynes (entries 13,14). A similar regioselectivity pattern had been observed earlier (e.g., data in ref. ^{1b,c 11}).

Typical experimental procedures: **A. (on adsorbents).** DCHCC of propyne **3** (0.63g, 1.9 mmol) in hexane (15 ml) was mixed with chromatography grade SiO₂⁹ (10.0 g). Solvent was removed on a rotovap and the resulting dry powder was added to a pre-cooled (-78°C) ampoule, charged with 0.3 ml (4 mmol) of methylenecyclopropane **1**. The ampoule was sealed, vigorously shaken, and heated at 50° for 2 hours (color changes from pink to gray). The content was thoroughly extracted with ether and, after ether removal and TLC separation, pure⁶ 6-methylspiro[2.4]hepten-6-one-5 (**6a**, 0.125g, 53%) and 5-methylspiro[2.4]hepten-5-one-7

(6b, 0.025g, 11%) were isolated as colorless liquids. **B. (on zeolites).** Zeolite H-ZSM (0.54g) was added to precooled (-78°C) hexane (2 ml) solution of **1** (0.17 ml, 2.3 mmol) and isopropenylacetylene (0.4g, 1.2 mmol). The sealed tube was then heated at 50° for 30 min. After usual work-up, 6-isopropenylspiro[2.4]hepten-6-one-5 (0.103g, 58%) and 5-isopropenylspiro[2.4]-hepten-5-one-4 (0.020g, 11%) were obtained as colorless liquids⁴.

Successful use of DSAC for the cycloaddition with **1** prompted us to check the applicability of this procedure for intermolecular Khand-Pauson reactions with other alkenes, namely, norbornene **8**, indene **9** and methylenecyclobutane **10**. In all these cases cycloaddition was found to proceed faster and with higher efficiency in comparison to the reactions run under traditional LPC.



While the effects observed for the examples shown in Scheme 2 are less pronounced than those observed earlier for intramolecular Khand-Pauson reactions⁴, they, nevertheless, clearly indicate the feasibility of DSAC as a possible alternative to conventional LPC procedure.

The origin of the described promotion effects of the various solid supports is not completely understood. However, one may reasonably suggest that it is mainly due to the interaction of the donor centers on the surface with alkyne DCHCC which facilitates the exchange of CO for alkene (e.g., **1**) ligand. Unfortunately, there is no direct experimental evidence in favor of this suggestion. However, its plausibility is supported by a plethora of data referring to the behavior of $\text{Co}_2(\text{CO})_8$ on the surface of solid supports (SiO_2 , Al_2O_3 , MgO , Zeolites), which indicated the easiness of ligand exchange leading to the formation of unstable surface bound cobalt complexes and to higher cobalt carbonyls³³.

The disclosed effectiveness of DSAC for such mechanistically different reactions as [2+2+1] cycloaddition⁴, Diels-Alder reaction^{14a} and Carrol rearrangement^{14b} clearly attests to the diversity of adsorption effects on the reactivity pattern of the organic compounds^{14c}.

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References

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5. Progress of the reaction was monitored by TLC (disappearance of colored non-polar spot corresponding to the starting DCHCC of alkyne).
6. Yields refer to the isolated products, their structure and homogeneity being ascertained by NMR, Ms and microanalysis data. Isomers a and b were separated by TLC.
7. Cf. to the data on the activity of various adsorbent in intramolecular Khand-Pauson reaction in ref⁴. See also: Smit, W.A.; Simonian, S.O.; Tarasov, V.A.; Shashkov, A.S.; Mamian, S.S.; Gybin, A.S.; Ibragimov, I.I.; Izvestia Acad. nauk, ser. Khim., 1988, 2796.
8. Variable amounts (yields 5-15% of the conjugated dienones of the general structure R¹CH=CHCOCH=C(CH₂)₂) also have been isolated. Their formation could be formally described as the acylation of **1** with vinylcarbonyl cobalt intermediates produced via initial hydroformylation of alkynes. This type of products has not been previously reported for Khand-Pauson reaction.
9. Chromatography grade adsorbents were used: SiO₂, L, 100/160μ "Chemapol," CSSR; Al₂O₃, acid, Poland; MgOSiO₂, Florisil, 75/150, Merck, BDR. In all cases the large excess of adsorbent is used (10-20 weight amount of that of substrates).
10. List of additional zeolites tested as the promoters in this reaction includes (in brackets are given SiO₂/Al₂O₃ ratios, time (min) necessary for the complete conversion of DCHCC at 50°C, yields⁶ of the respective cycloadduct (a+b)): Na-mordenite (10, 60, 52%); NaY (4.7, 60, 50%); K, Na-erionite (6.2, 120, 37%); Silicalite (1000, 30, 39%). Ratios SiO₂/Al₂O₃ for NaX and H-ZSM were respectively 2.6 and 40. Increased activity of the latter zeolite allowed to run the preparative cycloaddition with the reduced amount of the solid support (see procedure B).
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